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ELECTROCHEMICAL

EXPERIMENTS

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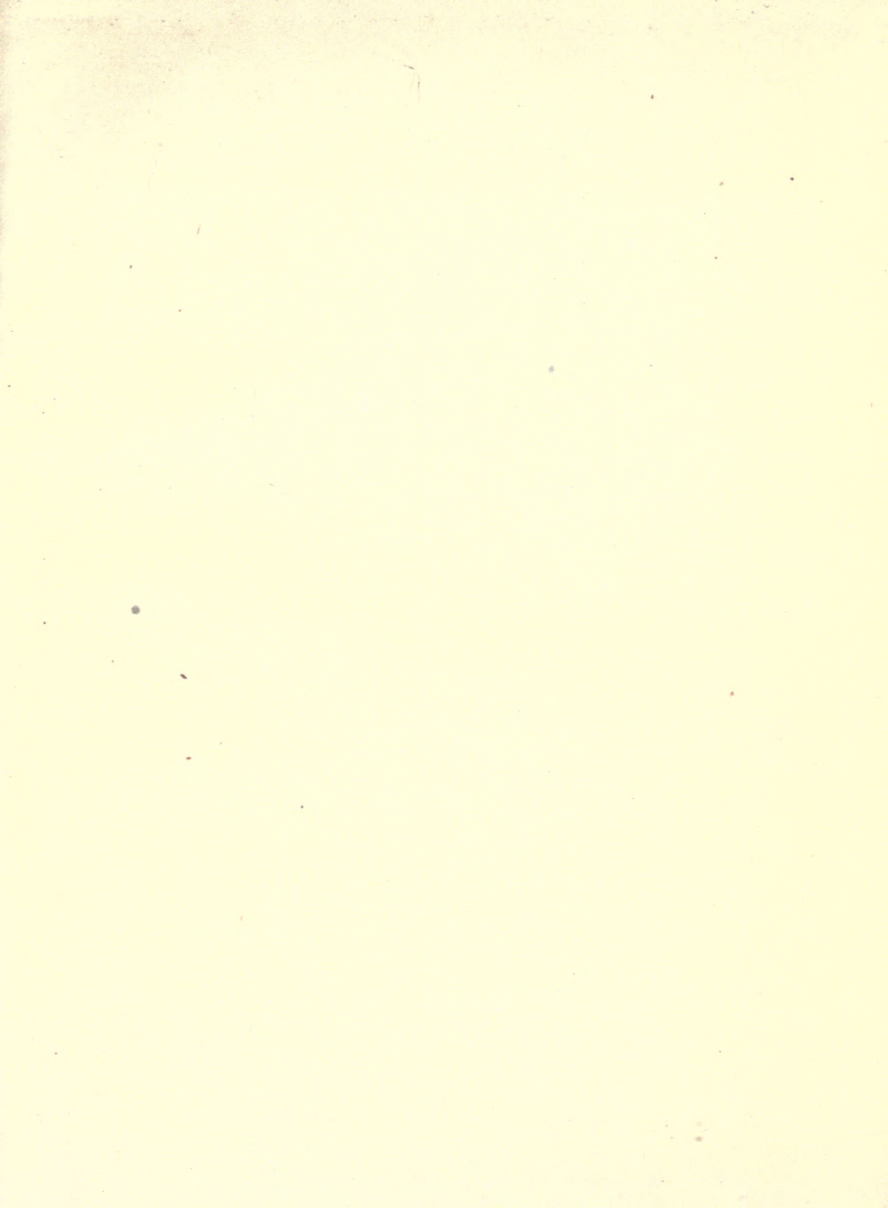


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INTRODUCTION
TO
ELECTROCHEMICAL
EXPERIMENTS

BY
DR. FELIX OETTEL

TRANSLATED
(WITH THE AUTHOR'S SANCTION)

BY
EDGAR F. SMITH



PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF PENNSYLVANIA

With Twenty-six Illustrations

PHILADELPHIA
P. BLAKISTON, SON & CO.
1012 WALNUT STREET
1897

QD 557

022

GENERAL

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PREFACE.

THE purpose of this little volume is to furnish technical chemists and all persons interested in the applications of electricity to chemical manufacture with a concise guide, containing in a compact form all that is essential for the comprehension and solution of problems arising in this comparatively new field of chemical investigation. That it has in a measure fulfilled its mission is evidenced by the hearty reception and favorable criticism accorded it in its German home, and by its translation into Russian. That it may prove equally helpful to all its English-speaking readers is the hope of the translator, to whom it is a pleasure to acknowledge indebtedness to Prof. George F. Barker for advice and assistance in the preparation of the text and correction of the proof sheets.

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INTRODUCTION

TO

Electrochemical Experiments.

A. SOURCE, MEASUREMENT, AND REGULATION OF THE CURRENT.

SOURCES OF THE CURRENT.

Four sources may be considered : ordinary galvanic batteries (primary batteries), storage cells or accumulators, thermopiles, and dynamo machines. The first are most readily obtained, but constitute a rather incomplete adjunct. Storage cells are decidedly more advantageous, so far as regards constancy of current and cleanliness in handling. Those who have employed this source of electric energy return to the ordinary battery only in cases of absolute necessity. Storage cells may be charged either by dynamos or by thermopiles. The latter were, for a time, deemed worthless, but since their improvement in construction have again come into favor. They are to be recommended for experimental work on a small scale,

and for analytical purposes, but are only available when illuminating gas can be had. A small dynamo is the best source of current for various practical experiments.

In undertaking an electrochemical investigation, the most rational beginning is the selection of the proper working conditions for the experiment, aside from batteries or accumulators. With the data and experience thus gained, the next step is the arrangement of a small plant provided with a dynamo. Difficulties, as a rule, now appear; these are generally of a constructive nature. When they have been surmounted, and the miniature experimental plant serves its purpose properly, calculations for some definite process may next engage the attention of the experimenter.

After this brief enumeration of the different sources of electric energy and their general application, a more detailed description of them may be given.

PRIMARY BATTERIES (GALVANIC CELLS).

Cells of this class, designed for the execution of electrochemical experiments, should furnish a strong and constant current. Many forms have been devised, but there is not one which fully meets these conditions, hence there can be no purpose in entering into a detailed description of each variety. Two may be mentioned—the Bunsen cell and the Daniell cell.

The *Bunsen cell* is the zinc-carbon combination.

It consists, usually, of a glass jar in which there is a heavy, amalgamated zinc cylinder (— pole). Within the latter stands a porous cup. This contains concentrated nitric acid, in which is immersed a bar of hard gas-carbon. The glass jar contains dilute sulphuric acid (1:20). The action of the current causes a reduction of the nitric acid, and fumes of nitrogen dioxide arise, making it necessary to keep the batteries in a good draught chamber. This inconvenience may be partly obviated by dropping into the cup, from time to time, chromic acid or potassium bichromate. The electromotive force of the cell is 1.8 V. At first the current from it is very strong, but it grows considerably less in the course of a few hours. This form of battery is very well adapted for experiments requiring a strong current for a relatively short time, and where high pressures are necessary. It is not suited for experiments extending through a period of days.

The following points should be observed when using this battery. The zinc must be well amalgamated, otherwise a tumultuous evolution of hydrogen will occur, leading to a rapid consumption of the zinc. In amalgamating, first dip the zinc cylinder into very dilute sulphuric acid, then pour mercury over it, and distribute the latter with a brush. The clay cup should not be so porous that much nitric acid can reach the zinc. In arranging the battery, the sulphuric acid is first introduced, and when the

porous cup has become thoroughly permeated with it, the nitric acid is introduced into the cup. As regards the carbon bars, it may be said that those from natural retort carbon are superior to those made from pressed carbon. To prevent them from absorbing nitric acid, which would eventually reach and destroy the metallic binding-screw attachments at their exposed ends, the bars should be heated or dried thoroughly and the ends then immersed in melted paraffin, the excess of the latter being removed with a brush. The binding screws, in union with the battery poles, should be clean and bright; the other parts may be covered with an asphalt paint, and in this way be protected from acid vapors. The current may be conducted from the battery according to the experiment by a stout copper wire (not less than one mm. in diameter). This is sometimes rolled into spirals, although there is really no necessity for so doing.

The *Daniell cell* possesses less electromotive force but greater constancy than the Bunsen cell. It consists of amalgamated zinc in dilute sulphuric acid, and copper in a saturated copper sulphate solution, the two liquids being separated by a porous cup. The sheet of copper serving as the positive pole is cylindrical in shape, and perforated. A copper wire is welded to it. In order to maintain a concentrated solution, a perforated bottom is sometimes placed in the upper portion of the jar. Crystals of copper

sulphate are, from time to time, placed upon it. If zinc be on the exterior and copper be placed in the porous cup, the combination will prove more energetic than with the reverse condition. The pressure of such a cell will be about 1.05 V. The nature of the porous cup affects the efficiency of a battery very much. If it be too dense, the internal resistance of the cell will be too great. If it be too porous, then the copper solution will penetrate to the zinc and the latter will rapidly become covered with a film of copper, in consequence of which the action of the cell will be much diminished.

In testing a porous cup, fill it, when perfectly dry, with water. It should be wet throughout within a few minutes, but the water should pass through it very slowly. It is a good rule to reject all porous cups which, shortly after they have been moistened, show drops of water on their external surface.

Another form of Daniell cell, arranged for continuous use, consists of a hollow zinc cylinder, not amalgamated, standing in a concentrated zinc sulphate solution. In the porous cup there is a copper cylinder immersed in a solution of copper sulphate. By use, the latter loses color, indicating that it is necessary to add crystals of blue vitriol. From time to time the zinc solution is siphoned off, an equal volume of water being added to prevent the separation of crystals of zinc sulphate. Once or twice every week the zinc cylinder should be taken out and

cleaned. An arrangement of this sort consumes very little zinc, but has a greater internal resistance. Its pressure does not exceed 0.9–0.95 V.

The disagreeable deposit of salts on the edges and over the sides of the cells can be lessened by employing porous cups with glazed edges, or by paraffining the portion of the cup extending beyond the liquid. It can not, however, be wholly overcome. When the battery is disconnected, the carbons and the porous cups should be thoroughly washed, and put away when dry. If the washing be omitted, the cups will be cracked—or at least be damaged to a marked degree—by the salts which crystallize out.

When a battery or cell is to be again put together, the cup must first be thoroughly saturated with the zinc sulphate solution, and the blue vitriol solution then be introduced into it. If the cup be not dry, but moist with water, it will, in consequence, yield but a feeble current until its walls are filled by diffusion with the better conducting vitriol solution.

ARRANGEMENT OF CELLS.

Having a number of cells, it is possible to arrange them in three different ways:

(a) *Parallel*, when all the zinc poles are connected with one another, and the copper poles in like manner (Fig. 1).

(b) *In series*, when each zinc pole is connected with the copper pole of the adjacent cell (Fig. 2).

(c) *In groups (mixed arrangement)*; an equal number of cells are united into groups and the latter then arranged as individual cells. The arrangement will

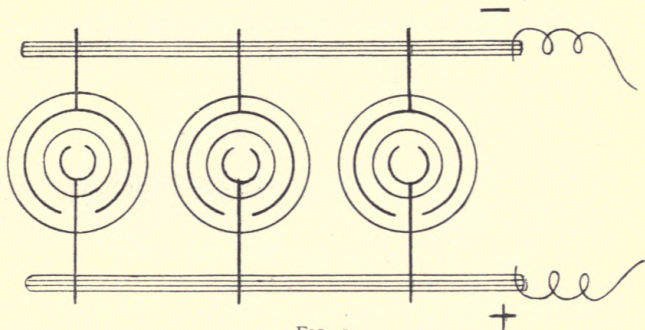


FIG. 1.

be different, depending upon whether that of (a) Fig. 3 or (b) Fig. 4 is observed within the group. The first is preferable, because slight defects in the individual cells are less disturbing.

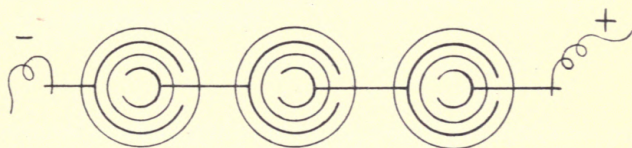


FIG. 2.

When should the one or the other combination be chosen? In answering this question, the following points should be remembered:

(1) The maximum work of a battery is obtained when the resistance in the outer circuit is equal to the total resistance of the battery.

(2) In the parallel arrangement of cells, the electromotive force of the battery is not altered. The inter-

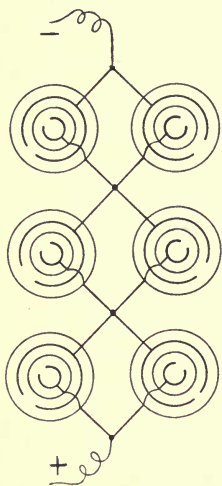


FIG. 3.

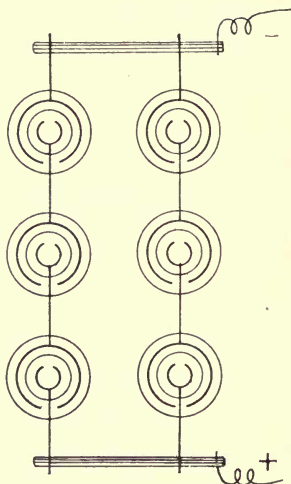


FIG. 4.

nal resistance is, however, diminished directly according to the number of cells.

(3) When cells are arranged in series, both the pressure and the resistance of the individual cells are increased in the sum total.

If the electromotive force of a cell be represented

by e , and its internal resistance by w , then a battery of n cells arranged parallel would have

the electromotive force e

and

the internal resistance $\frac{nw}{n}$.

A battery with cells in series would, on the contrary, have

the electromotive force $n \cdot e$

and

the internal resistance $n \cdot w$.

With a battery of n cells in series, composed of a elements parallel, each group would have

the electromotive force e

and

the internal resistance $\frac{nw}{a}$,

so that in the entire battery of n such groups there would be

the electromotive force $n \cdot e$

and

the internal resistance $n \cdot \frac{nw}{a}$.

According to Ohm's law, the current strength in a circuit is equal to the electromotive force divided by the total resistance. The latter equals the sum of the internal resistance W_i of the battery and the resistance

W_a of the external circuit, so that the current strength I may be expressed by the formula

$$I = \frac{E}{W_i + W_a}.$$

This formula gives two possibilities for the increase of current: either by increase of the numerator or the diminution of the denominator. The first follows from the arrangement of cells in series (increase of electromotive force), the second from their parallel arrangement (reduction of W_i). Which course should be pursued depends upon whether W_a is large or small in proportion to W_i . Several examples will serve to demonstrate that in cases of great external resistance a series arrangement of the cells is the proper arrangement, while with low external resistance the parallel arrangement should be chosen.

Examples:

The E. M. F. of a cell is 1.05 V.

Internal resistance of a cell is 0.5 Ω .

(a) External resistance is 10 Ω .

Current strength with various combinations:

$$1 \text{ cell, } \dots \dots \dots I = \frac{1.05}{0.5 + 10} = 0.10 \text{ amp.}$$

$$2 \text{ cells in series, } \dots \dots I = \frac{2 \cdot 1.05}{2 \cdot 0.5 + 10} = 0.19 \text{ amp.}$$

$$4 \text{ cells in series, } \dots \dots I = \frac{4 \cdot 1.05}{4 \cdot 0.5 + 10} = 0.35 \text{ amp.}$$

Reverse :

$$2 \text{ cells in parallel, } \dots I = \frac{1.05}{\frac{0.5}{2} + 10} = 0.102 \text{ amp.}$$

$$4 \text{ cells in parallel, } \dots I = \frac{1.05}{\frac{0.5}{4} + 10} = 0.104 \text{ amp.}$$

(b) External resistance = 0.1 Ω .

Current strength with various combinations :

$$1 \text{ cell, } \dots I = \frac{1.05}{0.5 + 0.1} = 1.75 \text{ amp.}$$

$$2 \text{ cells in series, } \dots I = \frac{2 \cdot 1.05}{2 \cdot 0.5 + 0.1} = 1.91 \text{ amp.}$$

$$4 \text{ cells in series, } \dots I = \frac{4 \cdot 1.05}{4 \cdot 0.5 + 0.1} = 2.0 \text{ amp.}$$

Reverse :

$$2 \text{ cells in parallel, } \dots I = \frac{1.05}{\frac{0.5}{2} + 0.1} = 3.0 \text{ amp.}$$

$$4 \text{ cells in series, } \dots I = \frac{1.05}{\frac{0.5}{4} + 0.1} = 4.67 \text{ amp.}$$

After some experience in electrochemical work it will be easy to determine whether one is confronted in an experiment with a high or low resistance, and the manner of cell arrangement will accordingly follow. Until such experience has been acquired, the safest, wisest course will be—to experiment! Intro-

duce a measuring instrument between the battery and the experimental cell, and vary the arrangement of the cells until the maximum current strength is obtained. The mixed arrangement will be found preferable if the cells employed, either in consequence of their small size, or from any other causes, show a high internal resistance. Several cells arranged in parallel will give the same result as one large form of like type.

Meidinger cells are frequently met with in laboratories. They are only suitable for analytical operations in which great current strength is not required. For electrochemical experiments of any other sort they are worthless, because too many of them must be arranged in groups to get currents of any great degree of intensity.

STORAGE CELLS, ACCUMULATORS,* SECONDARY BATTERIES.

While all primary batteries are more or less inconvenient to handle, and, as a rule, furnish currents which are not very strong, storage cells or secondary batteries are excellent sources of electric energy, and serve for the most varied electrochemical experiments.

Accumulators consist of a number of lead plates which are covered with a so-called "active mass."

* A clear, concise description of the action and care of secondary batteries will be found in Elbs' "Die Accumulatoren," Leipzig, 1893. *Hoppe*, "Die Accumulatoren," 2te Aufl., Berlin, gives a more exhaustive and historical account of their development.

On the anode (positive) plate this is lead superoxide, while on the kathode (negative) plate it is spongy lead. The liquid is pure, dilute sulphuric acid. Secondary batteries are, therefore, galvanic batteries, which, in consequence of lack of diaphragm, have a vanishingly low, internal resistance. When exhausted, it is not necessary to take them apart; for by contact with a more powerful source of energy they can be directly charged—*i. e.*, they can be again restored to their normal, useful state.

The various modifications found in trade are practically the same. Nearly all are guaranteed for a longer or shorter period. The Tudor and Correns* types are among the best. There are both stationary and transportable varieties; the latter are closed, so that no loss of acid occurs in transportation from one place to another.

The capacity of a storage cell is given in ampere-hours. The current strength varies with the individual types, and so long as it is not exceeded, it is immaterial how the electric energy is applied—*i. e.*, whether a powerful current is used for a brief period or a feeble current for a prolonged period. A storage cell with a capacity of 100 ampere-hours with a maximum current of 10 amp. may be discharged at the rate of

10 amperes for a period of	10 hours, or
5 " " " "	20 "
1 " " " "	100 " etc.

* The chloride accumulator is most widely known in this country.
—TR.

Most factories give instructions as to the manner in which their secondary batteries shall be handled. General rules may, however, be given here. The smaller types are usually mounted. The glass jars should be thoroughly cleaned without removing the lead plates. The latter are then completely immersed in pure, dilute, cold sulphuric acid of 1.15 sp. gravity. The purity of the acid is important. The presence of arsenic or nitric acid in it is harmful. If the acid at hand is not sufficiently pure, conduct hydrogen sulphide through it. Filter out the precipitated sulphides, and expel the hydrogen sulphide gas by means of an air current. When the glass jars have been filled, begin "charging." Connect the brown + plates with the + conducting wire of a dynamo (or a thermopile) and the gray — plates with the — pole. The current recommended for the cell, by its manufacturer, is next conducted into it. As a rule, this first charging will extend through a day or more. It is in this way that the plates are first brought into normal condition. The current will, apparently, be taken up completely by the accumulator. The + plates gradually change in color to a brownish black, while the — plates become a light gray. Eventually, a strong evolution of gas will be observed, first on the positive and later on the negative plates ("the acid boils"). When the evolution of gas on all the plates remains nearly the same for an hour, the first "charge" may

be regarded as finished. The pressure for each cell will have increased to 2.5 V.; the specific gravity of the acid will vary from 1.15 to 1.18–1.20. All of the active mass upon the positive plates will now be completely oxidized, and that upon the negative plates will be fully reduced. The first discharging can next follow. It should be done with the current strength previously mentioned. The pressure will fall rapidly to 2.0 V. and then remain constant for a long period. As soon as it decreases to 1.85 V., the discharging should be interrupted. The cells should then be charged a second time until the pressure reaches 2.5 V. and equal gas evolution is observable on all plates. The cell is now ready for further use.

To insure long life to the cell, certain precautions should be observed :

1. It must be preserved from "short-circuiting."
2. The maximum strength of the discharging current must not exceed that given by the manufacturer of the cell.
3. Do not discharge below 1.85 V.
4. It should not continue long in a discharged condition. If not wanted for use, it should be held in a charged state.
5. It is well occasionally to *overcharge*—*i. e.*, to continue charging for some hours with a feeble current even after the "boiling" has begun.
6. Should it become necessary at any time to remove a plate from the acid, it must not be allowed to

become air-dried. It should be immediately immersed in dilute acid.

7. Avoid heavy blows: they loosen and throw out the "active masses."

By observing these rules, storage cells can be kept in satisfactory condition for some time, especially if the maximum effect be not constantly aimed at. It is better to charge too frequently than not enough. In time the surface of the liquid will sink below the upper edge of the plates. Pure water should then be added. The specific gravity of the acid should be taken after charging and discharging. The use of the hydrometer will furnish a means of ascertaining how far the charge has been consumed. If, in time, it is noticed that, after charging, the specific gravity of the liquid is not the same as was observed at first, when the cell was in this condition, it is evidence that acid has been lost by spattering or in some other way. Dilute acid should be added several times for the water that evaporates until the normal condition is restored.

Storage cells answer well, both for analytical and experimental purposes. The current and pressure of any source of electricity can, by this means, be altered in various ways. For example, a small dynamo of 5 V. and 30 amperes, together with six accumulators, each having a maximum discharge of ten amperes, are at the disposal of the operator. As the machine is only capable of charging $\frac{5}{2.5} = 2$ sec-

ondary batteries in series, groups of three cells each in parallel are formed, and these then connected in series to the machine. When the charging is finished, the following groupings may be made:

1 to 6 in series	will yield	2-12 V.	and	10 amp.
1 " 6 parallel	" "	2 V.	"	10-60 amp.
2 \times 3	" "	4 V.	"	30 amp.
3 \times 2	" "	6 V.	"	20 amp.

Accumulators have found their way into laboratories slowly because dynamos with which to charge them were rarely present. Recently, thermopiles* have been used successfully for this work, hence there now remains no good reason for their non-adoption generally in electrolytic work.

THERMOPILES.

Thermopiles, which transform heat into electricity, would be the most convenient sources of electric energy for laboratory purposes if they could be built in durable forms. In this respect the older modifications of Noë and Clamond were sadly lacking. They required much attention and a constant gas pressure, and, in spite of all care, rarely lasted for any great length of time. The new modifications of Gülcher† show decided improvement over the early types, and the common verdict in regard to them is very favorable. Julius Pintsch, Berlin, O., Germany, makes

* Elbs, Chem. Ztg., 1893, 66.

† D. R. P., No. 44146.

three varieties of this thermopile (Fig. 5). The largest model, consuming 170 liters of gas per hour, develops an electromotive force of 4 V. with an internal resistance of 0.6 to 0.7 Ω . The price of this form is about \$48. The smaller models consume 130-70 liters of gas, and have a pressure of from 3-1.5

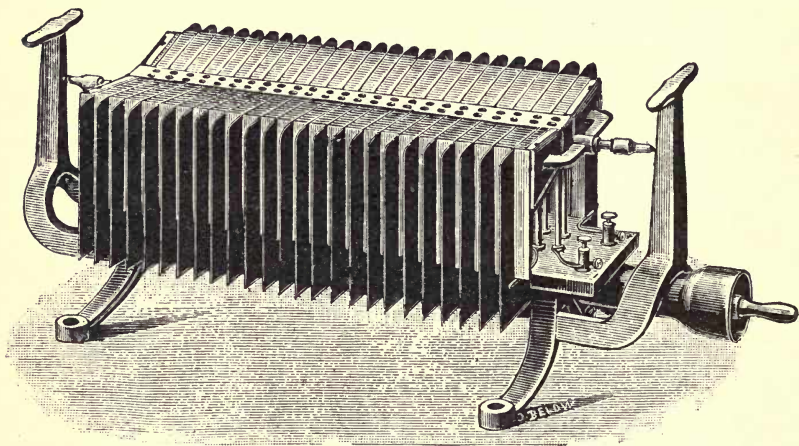


FIG. 5.

V. If it be desired to use the larger form for charging storage cells, the latter should be arranged parallel. This will result in the production of a current of from 2-3 amperes. For ordinary purposes, therefore, a thermopile of this description will be ample. At present they are used in laboratories

chiefly for electrolytic analyses, but combined with secondary batteries can be more widely applied.

DYNAMO-MACHINES.

The dynamo is the proper source of electric energy in all experiments requiring a powerful current for an extended period.

The action of such machines is dependent upon the electric current induced in a coil of wire when brought into a magnetic field—*i. e.*, when it is rotated between the poles of a magnet. The portion that is rotated is called the armature. Externally it has the form of a flat ring or cylinder. The magnets about which the armature rotates are not permanent, but are electromagnets excited by a part of the current produced by the machine. The several current impulses induced in the armature are collected in the commutator, or collector, and are given up by the brushes to the external conductors.

Two large classes of dynamos exist: direct current machines, and those producing alternating currents. In the first class, two successive current impulses have the same direction, while in the second class they proceed in opposite directions. For electrochemical purposes, direct current machines are alone of consequence.

The manner of winding also causes a division into series machines, shunt machines, and compound machines. In the first, the current produced in the

armature proceeds immediately about the electromagnets, then through the external circuit back to the armature. In the second, the current divides itself in the armature. The smaller portion of it proceeds about the electromagnets, while the major portion passes through the external circuit. In the mixed or compound machines, a part of the winding lies in the shunt circuit, the remainder in the main circuit.

Shunt machines alone interest us. They have this important advantage, that in consequence of any disturbances the poles can not reverse. They will, therefore, be somewhat more closely considered. As an example, or type, the Schuckert * flat-ring machine (Fig. 6) may be mentioned.

The current circulating in the external circuit is the *main current*, that about the magnets is the *shunt circuit* of the machine. The latter is interrupted at one point for the introduction of the shunt-regulator, *N*. This serves to change the pressure at the terminals of the machine. If resistance be introduced by means of this regulator into the magnet winding, the current passing through it will be less than before; consequently the magnetism and the magnetic field of the machine will be reduced and the pressure will fall. By suitable winding of the shunt regulator the pressure may be varied within wide limits. Another means of altering the pressure consists in changing the velocity. When the latter is increased, the pres-

* In this country the Edison machine is generally used.—TR.

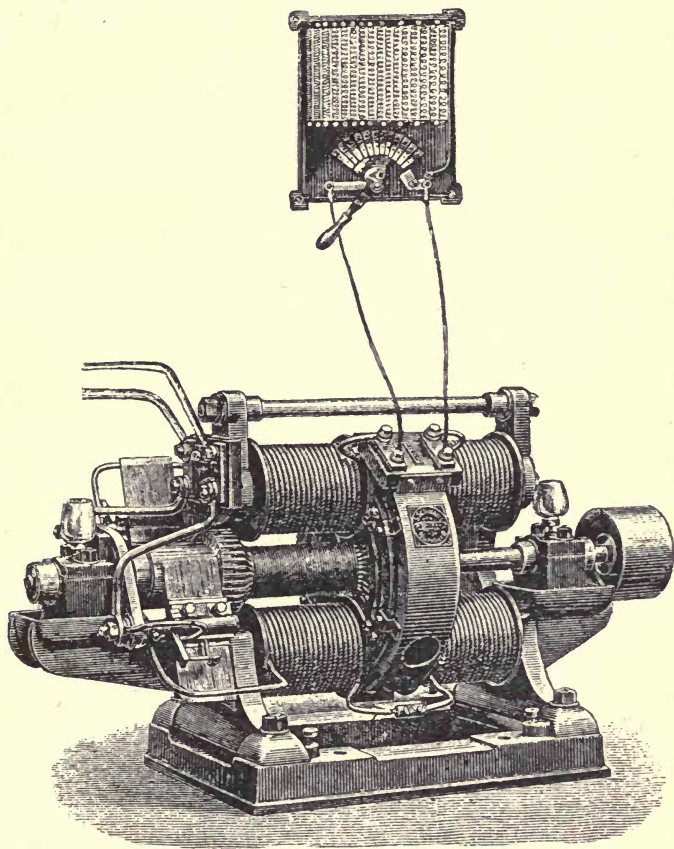


FIG. 6.

sure increases, and *vice versa*. This course is resorted to only when extraordinary conditions prevail, otherwise the velocity allowed by the builder of the machine must be taken as normal. A dynamo with an external resistance of 0.068 Ω will yield

125 Amp.	—	8.5 V.	—	with 500 revolutions.
215 “		14.7 V.	“	800 “
280 “		19.0 V.	“	1000 “

Dynamos are constructed for the most varied current strengths and pressures. In chemical operations, strong currents are of prime importance—the pressures are relatively low. Chemical dynamos vary, as a rule, from 4–20 volts and 100–500 amperes. For electric lighting the customary pressures vary from 65–110 V., while the current strength falls below 100 amperes.

The product obtained by multiplying together the voltage and the amperage represents the output of a dynamo. The number of volt-amperes is, therefore, a direct means of measuring the mechanical power of a dynamo in each moment of its activity.

A chemical dynamo “running empty,” *i. e.*, when it is not connected with a current circuit, rapidly attains the pressure allowed by its prevailing velocity. This is called the open-circuit pressure. It is always greater than that observed when the machine is doing work, or than the pressure on closed circuit. A wire resistance connected with the two terminals at once

shows a current, which may be calculated from Ohm's law. According to the latter, the current strength I is

$$I = \frac{\text{E. M. F.}}{\text{Sum of the resistances.}}$$

The electromotive force is the pressure of the machine. The resistance is on the outside—the resistance W , while within the machine there is the resistance of the armature A and the resistance of the magnet coils M . These two latter resistances are arranged parallel because the dynamo is a shunt machine. Together they equal $\frac{A \cdot M}{A + M}$; hence the equation for the current strength is

$$I = \frac{E}{W + \frac{A \cdot M}{A + M}}$$

By lowering the external resistance, the current increases and the pressure falls. The product of the pressure and current strength—the output of the dynamo—approaches the maximum. By further reduction of the external resistance the pressure will fall still further; the current will increase for a short period, but will then decrease until, with no external resistance (by short circuit of the dynamo), it becomes zero. The machine then furnishes no current. The voltage and amperage also rapidly drop from their maximum to zero.

This action is related, too, with the flow of current toward the limbs of the magnet. So long as the external resistance is great in comparison with the resistance of the armature of the magnet, so long will the greater portion of the current follow the more convenient path about the electromagnets. It will powerfully excite these, and acquire, in consequence, a high pressure. As the external resistance gradually grows less, the current which flows about the limbs of the magnet will be diminished, the magnetic field of the machine will become less powerful, also its efficiency, so that, eventually, when the external resistance has, by short circuit, fallen to zero, a current will no longer flow about the magnets, and the machine will cease to work.

The maximum work of a dynamo is attained when the external resistance is slightly greater than its internal resistance. This condition is the basis for the normal work given by the manufacturer of the machine.

Smaller machines, intended for experimental purposes,—models,—are constructed with two separate circuits. These carry a double coil upon the armature. The main coil, with low resistance, gives up its current through the main brushes to the external circuit; the other coil has greater resistance, and the current developed therein is delivered to the magnets altogether in the side brushes. There are also machines with separate magnet excitation. Should

short circuiting be produced in such machines by carelessness, the only resistance in the entire circuit would be the main armature, and all the energy of the machine would be consumed in bringing this resistance to such a state that it would ignite. In other words, the armature would be burnt out and the machine be ruined. Direct current machines and compound dynamos are damaged in the same manner. It is only the true shunt machine that is non-sensitive.

The natural desire on the part of any one considering the introduction of a small dynamo, is that it shall be suitable for every possible purpose. This wish can not, of course, be wholly realized. It can not be expected that one and the same machine will serve both for electrolysis and fusion purposes, because, in the first instance, low pressure and high current are required, while in the second case the requirements are directly the reverse—high pressure and moderate current. It is always well to have sufficient pressure, as it can be easily reduced, but it is increased with difficulty. But few electrolytic operations require more than 5 V. pressure, so that this, in most cases, would be amply sufficient ; yet, to render the machine as widely useful as possible, it is well to double this power for the following reason.

In all technical operations, this question must be constantly kept in view : How can this work be done on a technical scale? The work of a dynamo can, however, only be doubled by increasing the current

strength or by increasing its pressure. Reasons, to be given later, will show that the latter course is preferable. However, to consume or exhaust the highest pressure the electrolytic baths must be arranged in series, as in the case of primary batteries. But with this arrangement, phenomena frequently present themselves which are not noticeable in a single bath. If the machine, then, has a direct pressure of 10 V., it is even possible, with a counter bath pressure of 5 V., to try series arrangements. With baths of lower pressure, it is, of course, understood that there can be more baths arranged in series.

A machine having a pressure of 10 V. and a current of 70–100 amperes will satisfy the greatest demands which can be made upon a dynamo intended for electrolytic experiments. The energy consumption will, therefore, equal from $1\frac{1}{2}$ –2 H. P.

RULES FOR THE ARRANGEMENT AND RUNNING OF SMALL DYNAMOS.

The machine should stand upon a solid foundation, which can not be easily shaken. When possible, this should be a pier about $\frac{1}{2}$ m. in height. It will render the observation of and attention to the brushes much easier. It would be very convenient and practicable if the dynamo stood upon rails which would permit of its movement in the direction of the driving belts. Such a shifting is the simplest and most convenient means of stretching a belt that has become loose and

flabby; cutting and sewing anew would otherwise be necessary. An arrangement permitting this can be furnished for every machine upon mere request to the maker.

The transmission is best provided with a triple cone pulley, so that the middle step affords the normal number of revolutions, and the other two a somewhat higher or a lower number. Avoid covered driving belts.

The bed of the machine should be kept well lubricated. The "self-oilers" should always be full. The brushes should fit lightly but closely. When the collector is pressed too closely it is unnecessarily abraded and heated. To insure long life to the collector, it should be constructed from hard bronze, while the brushes should consist of soft copper. The writer's experience warrants the statement that brushes from sheet metal are superior to straight or twisted wire. They consist of rolled sheets, thin as paper and soft as feathers, which slide along the entire width of the collector. In consequence of their great elasticity and the absence of any points, such brushes do not spark, and the collector continues smooth for quite a long period.

New brushes are brought in contact with the collector when the dynamo is running empty. Projecting points produced by wear should be cut off, because they rapidly damage the machine. The brushes in action require careful attention. When sparking sets

in, the binding screws should be eased and the brushes withdrawn until the evil is corrected. In this adjustment care must be taken not to raise the brushes from the collector during the revolution of the latter. The consequence of such an act would be not only the production of a blinding spark, but, in all probability, a very severe shock. In disconnecting the main current avoid interrupting the conductors with both hands, thus introducing the body into the circuit. This always induces heavy shocks. In other respects the various parts of a dynamo can be handled during its action without experiencing any unpleasant sensation.

When the collector has become rough and worn, the brushes are removed, and it is polished with emery paper. When great inequalities exist, a smooth file may be used, or the collector may be made to revolve around a sharp file.

The abrasion of the brushes and of the collector gives rise to a fine metallic dust which deposits on all parts of the machine. It must be removed at intervals. This is done, in the case of portions more difficult of access, by use of a bellows. Gentle tapping displaces it from the brushes. Copper dust should not be allowed to accumulate on the collector or its connections with the armature; it gives rise to short circuits in individual segments.

The current is best conducted to the baths by flat metallic sheets of ample section. Branches are more conveniently made from these than when rods of

metal are used. Their connection with the machine is made with strips of copper cord, so arranged that the machine is still movable on its foundation.

CURRENT MEASUREMENT.

Two courses may be followed in measuring currents. The chemical action of the electric current (voltameter) or its magnetic action upon a conductor through which it passes (galvanometer) may be used for this purpose. To determine the current strength in a circuit, *i. e.*, in an experiment, it is well to insert one of the instruments just described into the circuit, which consists of: battery—experiment—measuring instrument—battery. It would be wholly wrong to have the following succession: battery—instrument—battery, and then assume that the current strength thus observed was identical with that from the arrangement: battery—experiment—battery.

Electromagnetic measuring apparatus is calibrated in an entirely empirical way by means of voltmeters, therefore the latter will be the first to receive a brief description. Voltmeters are based upon Faraday's law, which reads: "The same current in equal units of time decomposes equivalent quantities of chemical compounds." As representatives of the latter, we may choose silver nitrate, copper sulphate, or dilute sulphuric acid, and then determine the quantities of metallic copper, metallic silver, or electrolytic gas sep-

arated in a definite period of time. Consequently, we distinguish silver voltameters, copper voltameters, and the oxyhydrogen voltameters. Certain precautions must be observed with each to obtain accurate results.

SILVER VOLTAMETER.

This is regarded as the most accurate voltameter. Secondary reactions do not occur in it. The high equivalent of silver, and the fact that very considerable quantities of metal are precipitated by comparatively feeble currents, reduce the error in weighing to a minimum. A disadvantage which must be recognized is that silver is greatly inclined to separate in crystals, which are loosely attached to the kathode. Consequently, stronger currents can not be sent through the apparatus without the possibility of some of the deposit becoming detached. In measuring strong currents with this instrument, electrodes with a sufficiently large surface must be provided, besides which the current should not be allowed to act for more than one to two minutes.

The voltameter usually consists of a silver or platinum dish serving as a kathode, in which there is a moderately concentrated neutral silver nitrate solution. The anode, of pure silver, is a pencil dipping into the liquid. This anode is surrounded by a muslin bag serving to collect any particles of silver which may separate, thus preventing them from falling upon the dish and so falsely increasing the weight of the latter.

A more convenient form of this voltmeter consists of a small beaker glass containing the silver solution. A sheet of pure silver serves as the anode, while the kathode is a plate of platinum. The liquid should be agitated with a glass rod during the action of the current. Finally, the platinum plate is removed, rinsed with water, dried, and weighed. If, after several experiments, the crystals have become so large that they threaten to fall off, clean the platinum plate by immersion in nitric acid.

A current of one ampere precipitates

0.001118 gram Ag in one second, or
0.06708 " " " " minute.

COPPER VOLTAMETER.

In this instrument the electrodes are two copper plates of equal surface. The thicker of the two serves as the anode, the thinner plate as the kathode. They dip into a solution of copper sulphate. In this instance, also, the liquid should be thoroughly agitated during the action of the current. The precipitated copper should have a bright red color and be perfectly adherent. It is first dipped into water, then into alcohol, after which it is dried over a flame. When strong currents are used anodes are placed on both sides of the kathode.

Early data indicate that, as a filling liquid, an almost saturated and perfectly neutral copper sulphate solution answers best. It, however, increases the

resistance of the voltameter, in consequence of which a relatively high pressure will be required. Furthermore, low results arise when feeble currents are employed, because then the copper which separates contains cuprous oxide. It has been shown* that perfectly exact values, agreeing with those obtained by the silver voltameter, have resulted by using current densities varying from 0.06 to 1.5 ampere for a sq. dm. of kathode surface. This was done by the employment of the following solution :

15	grams of	crystallized copper sulphate.
5	“ “	concentrated sulphuric acid.
5	c.c.	“ alcohol.
100	“ “	“ water.

The pressure (0. 1 — 0. 5 V.) is only half as large as that required for the neutral liquid.

Such an arrangement of the copper voltameter is well adapted for most practical requirements. Its results are correct. It is inexpensive and easily made, and, in addition, can be thrown into a circuit for almost any length of time. It can also be used with advantage as an ampere-hour meter (see p. 51).

One ampere of current precipitates 0.0197 gram of copper in a minute, or 1.181 gram of copper per hour.

THE OXYHYDROGEN VOLTAMETER.

In this voltameter dilute sulphuric acid (sp. gr. 1.1–1.2) is decomposed between two platinum

* Chemiker Zeitung, 1893, 543.

plates. The resulting electrolytic gas is measured. An ampere liberates 10.44 c.c. of electrolytic gas (at 0° and 760 mm. pressure) per minute. This kind of voltameter is convenient, because it does away with all weighings. The reduction of the volume of gas

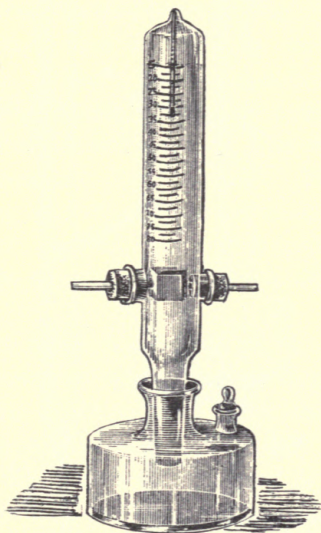


FIG. 7.

can be taken from tables, and in a few minutes the apparatus will again be ready for a new measurement.

This convenience, however, is offset by the disadvantage that the pressure required by the voltameter is high. It varies from 1.7 to 2.5 V. according to the

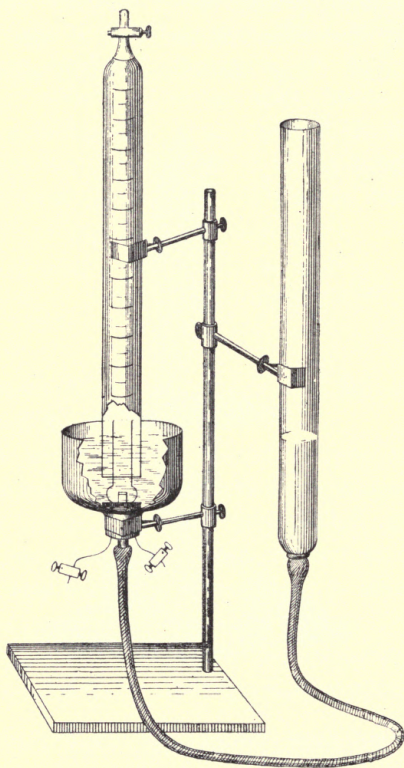


FIG. 8.

size of the instrument. Therefore, to ascertain the current strength in an experiment which demands a pressure of 4 V., it would be necessary to employ some source of electric energy with a pressure of about 6 volts!

If an oxyhydrogen voltameter is to be used, the modification made by Kohlrausch (Fig. 7) is preferable. The eudiometer vessel is filled by merely inverting the apparatus. What is known as Schmitt's nitrogen eudiometer (Fig. 8) can readily be converted into a practical electrolytic voltameter. The electrodes are introduced through rubber stoppers. The measuring burette, during use, is pushed somewhat above the rubber stopper. In reading, it is placed on the latter and brought to equal pressure by the adjustable leveling tube.

Voltameters of this description are only in rare cases adapted for current measurement by introduction into the circuit. In order to read them the experiment must generally be interrupted, and they augment the resistance of the circuit to a marked degree. These inconveniences may be avoided by the use of measuring apparatus based upon electromagnetic principles. These will now be described. The

TANGENT GALVANOMETER

is the simplest example of its class. It consists of a circular heavy copper wire. A magnetic needle, attached to an unspun silk fiber, oscillates in this ring

over a graduated circle. The plane of the ring is placed in the meridian in the direction of the needle. The latter is short, compared with the diameter of the ring (not more than one-sixth). The magnetic strength of the needle does not affect the measurement. When the needle is short, a more accurate reading can be obtained, even when there is a large divided circle, by attaching to the needle a lighter and longer indicator.

When the needle is deflected α° out of the meridian, the current strength will be

$$I = c. \text{tang. } \alpha.$$

Here, c indicates a constant value for each instrument.

To determine this constant c of the galvanometer, introduce the latter, together with one of the voltmeters, just described, into the circuit of some constant source of electric energy (the order being: battery—voltmeter—galvanometer—battery). Close the circuit for a few minutes, note the average deflection, and from the reading of the voltmeter calculate the current in amperes. If, with a deflection of α° , the current strength was found to be I amperes, the constant sought will be

$$c = \frac{I}{\text{tang. } \alpha}.$$

Several such experiments are made with varying currents, and from the mean thus found the value for c is taken. A table is then calculated once for all to

serve for the different deflections. To alter the current strength, an additional cell is added, or a German silver wire is introduced into the circuit as resistance.

Gauguin has made a modification of the tangent galvanometer in which the magnetic needle does not swing in the center of the ring, but is shifted from the circular plane one-fourth of its diameter. The length of the needle can now be increased without producing a variation from the law of tangents.

Having constructed a table for the galvanometer, it will soon be observed that the measurements between 60° – 90° are uncertain, because for each degree of deflection the increase in current will become greater. It is not well to exceed 65° . In measuring larger currents, two courses are open: either a second galvanometer is used, which, with equal length of needle, has a larger ring diameter, or, a so-called shunt is introduced.

When two points in a circuit are connected, not by a single wire, but by two wires of different resistances, the current strength in the two wires will be inversely as the resistances. For example, when the current I between the two points A and B (Fig. 9) meets the two wires I and II with the resistances W_1 and W_2 respectively, it divides itself into the two currents i_1 and i_2 , between which the following relations exist:

$$1. \quad i_1 + i_2 = I.$$

$$2. \quad i_1 : i_2 = W_2 : W_1.$$

If, for example, the resistance W_1 is one-third that of W_2 , then three times as much current will flow through the former as through the latter, or, when referred to I , it would be: $i_1 = \frac{3}{4} I$ and $i_2 = \frac{1}{4} I$. On introducing, therefore, a galvanometer into a circuit and connecting its terminals by means of a wire, it will be possible, through the resistance of the selected wire, to deflect the major portion of the entire current through this shunt and to convey any desired fraction of it through the galvanometer. In

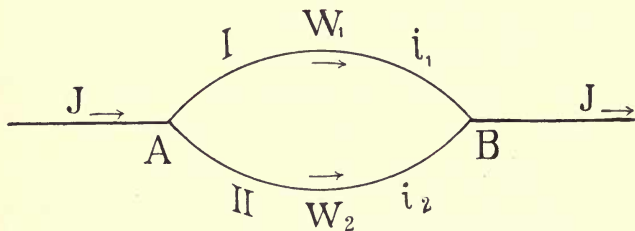


FIG. 9.

this manner the capacity of the latter is correspondingly increased. If the shunt has a resistance equal to that of the galvanometer, this would receive but one-half of the total current, hence its readings should be doubled. If, in general, the resistance of the shunt is $\frac{1}{n}$ of that of the galvanometer, the readings must be multiplied by $n + 1$. When, on the other hand, it is desired to conduct $\frac{1}{n}$ of the total current through the galvanometer, a shunt having $\frac{1}{n-1}$ of

its resistance must be introduced. If the resistance of the shunt is not accurately known, the correct readings of the galvanometer can be ascertained by a re-calibration with a voltmeter. The wire used as shunt must not be stretched out straight, otherwise the current passing through it will influence the needle. It should be doubled and then coiled up. In adjusting a galvanometer, care must be taken that adjacent currents do not influence it. Consequently, it is connected to the main circuit by two long wires, lying closely together, so that their inductive action can be disregarded.

By the aid of a shunt it is possible to employ very sensitive galvanometers, having many turns of wire (multipliers or galvanometers), for the measurement of current strength. The readings of such an instrument can not be deduced directly from a simple formula, but the instrument itself must be calibrated throughout its entire range with a voltmeter (p. 106).

TORSION GALVANOMETER.

The torsion galvanometer of Siemens and Halske (Fig. 10) is an exceedingly delicate instrument, and for exact measurements is almost indispensable. A bell magnet, provided with copper damping, is surrounded by a coil of many turns, and attached to a spring, by whose rotation the deflection of the magnet is compensated and restored to its original position.

The magnitude of the angle of torsion, therefore,

serves as a means of measuring the current passing through the instrument. The divisions are so selected that the wire coils have a resistance exactly equal to 1Ω , and one degree of deflection corresponds to 0.001 amp. With a shunt of $\frac{1}{9} \Omega$ the reading must be

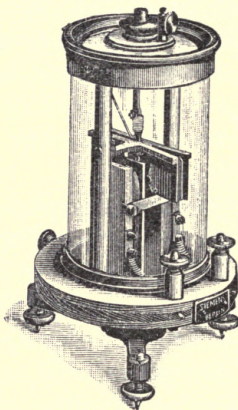


FIG. 10.

multiplied by 10; *i. e.*, 1° corresponds to 0.01 amp.; analogously, with a shunt of

$$\begin{aligned} \frac{1}{99} \Omega : 1^\circ &= 0.1 \text{ ampere,} \\ \frac{1}{999} \Omega : 1^\circ &= 1 \text{ ampere.} \end{aligned}$$

As the greatest torsion angle equals 170° , it is possible, with such an instrument and the three shunt resistances, which have been mentioned, to measure

currents ranging from 0.001–170.0 amp., which is, obviously, a very wide range.

MEASURING INSTRUMENTS FOR TECHNICAL PURPOSES.

These instruments carry an empirical scale, which gives direct readings in amperes. The instruments themselves can be constructed for all current strengths, but their range can not be read with the same degree of accuracy throughout. The first divisions are usually contracted; hence their readings are less reliable. Technical instruments of this class, called amperemeters, are indispensable for the control of work in a manufacturing establishment. They give a reading of current strength in amperes at any moment. They should always be introduced into the main circuit leading from the source of the current to the electrolytes. As most amperemeters are entirely independent of the direction of the current passing through them, it is immaterial whether they are connected with the negative or positive conducting wire.

Two phenomena, as a rule, are utilized in their construction: (1) A solenoid, through which the current passes, tends to draw an iron rod into its center; or, (2) a solenoid attracts an eccentrically arranged strip of sheet-iron toward the periphery. The two attractive forces are opposed, either by gravity or by the action of a spring. The modifications of this apparatus are almost innumerable. Two typical forms will be described:

The *spring-galvanometer* of Kohlrausch (Fig. 11) consists of a vertical solenoid. In it there is suspended a hollow sheet-iron cylinder, to which a spiral spring is attached. When the current passes through

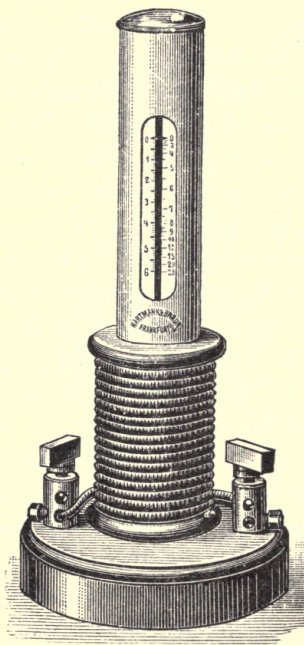


FIG. 11.

it, the iron cylinder is drawn into the solenoid until equilibrium is established by the extension of the spring. The latter then causes an indicator to move

over a vertical scale. The compact form of this instrument recommends it.

The amperemeter of Hummel (Fig. 12), though one of the earliest constructions, is yet one of the best. The solenoid in it lies in a horizontal position. It carries eccentringly a thin sheet of iron also in horizontal position, bent and fixed at certain points. It is provided with a long index, vibrating before a scale. The index nearly balances the weight of the iron strip, so that the sensibility of the instrument is

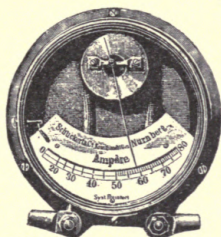


FIG. 12.

rather great. The absence of magnets and springs, as well as the convenient and accurate arrangement of the apparatus on the zero-point, when it is mounted, contribute much to making this a trustworthy amperemeter. Its calibration is generally reliable.

AMPERE-HOUR METER.

The electrolytic processes, proceeding quantitatively according to any single reaction, are few in

number. The majority are accompanied by secondary changes which represent more or less loss in work. Hence a prime factor in every electrolytic process is the determination of the current efficiency; *i. e.*, the ratio of the current active in the desired direction to the total current passing through the experimental cell. This demands an arrangement allowing the measurement of the amount of current which passes through the circuit in a definite period, and which is independent of the fact, whether the current strength has varied during the period of observation, or whether periods of cessation have actually occurred.

This essential can be realized in two ways: By use of the electromagnetic and the chemical action of the current. Aron applies the first means in his registering amperemeter. Two synchronous clocks are used: one has an ordinary pendulum, while that of the second is controlled by an electromagnet. Consequently, during the passage of the current, a time difference will be noticed in the reading of the two clocks, from which the amount of current, which has passed through the instrument, can be calculated. This apparatus is extensively employed in measuring the current consumed in electric light plants.

The amperemeter of Kohlrausch can be re-arranged so as to serve for the purpose of an ampere-hour meter. This may be accomplished by attaching a colored pencil to the indicator and allowing it to write upon a strip of paper regulated in its move-

ments by clockwork. All the variations in the current are recorded in this way. The surface traversed by the pencil represents the ampere-hours.

The copper voltameter described on page 39 can, without much expense, be changed into an ampere-hour meter. It should be retained continuously in the circuit. A glass or earthenware vessel will serve to contain the electrolyte. The anodes should be copper plates varying from 3 to 10 mm. in thickness. A thin copper plate will answer for the kathode. It should be weighed before and after the experiment upon an ordinary balance. One ampere-hour corresponds to 1.18 grams of copper. If the electrolyte is well agitated during the experiment, as much as $2\frac{1}{2}$ amperes can be allowed for 100 sq. cm. of smooth kathode surface. The liquid may be agitated either by a small stirrer or by conducting a stream of hydrogen gas through it. It is not advisable to blow air through, because sulphuric acid containing air oxidizes copper, and the results will, consequently, be inaccurate.

MEASUREMENT OF PRESSURE.

Ohm's law is thus expressed: $E = I \cdot w$. From this it is evident that every pressure measurement can be referred to a current measurement. To ascertain the pressure E , prevailing at the points A and B of a circuit, a shunt with a resistance w , should be at-

tached to them, and the current in this branch be then measured. The chief condition is that the quantity of current passing through the shunt should be an exceedingly small fraction of the main current, hence w must be very large in proportion to the resistance of the main current between the points A and B. The reason for this is very evident. By the attachment of the shunt, the resistance of the conductors between the points A and B is reduced, because the current has now two outlets. The smaller the resistance of the shunt, the more will the total resistance A B be diminished. To produce the original current strength in the now smaller resistance, a lower pressure than at first will be required; hence, by the introduction of the shunt, the pressure is changed, and is, indeed, lowered; or, in other words, *low pressures are obtained with the aid of a shunt of relatively less resistance*. The greater the resistance of the shunt, the less will the total resistance between A and B be altered, and, therefore, the more accurately will the pressure be determined.

The instrument for the measurement of pressure—the *voltmeter*—is, therefore, an amperemeter for very low currents. It possess a high resistance in itself, or a great resistance is inserted before it. Its divisions, empirically deduced, do not correspond to the current strengths which the individual deflections produce, but they are the product of these current strengths and the total resistance of the instrument;



i. e., I. w, which represents the pressure according to Ohm's law, expressed in volts.

Every sensitive galvanometer may be calibrated to do the work of a voltmeter by the insertion of a sufficiently large resistance (p. 111). The capacity of every voltmeter can be doubled by the insertion of a resistance equal to that of the instrument itself; and when the resistance is twice as great, the capacity is trebled, etc., etc.

The methods of pressure measurement, which are determined by the comparison of an unknown electromotive force with that of a normal element, can be omitted here, as they are all rather inconvenient. The chemist, engaged in electrochemical work, must be able to know, in a very few minutes, both the pressure and current strength, either by deflection of a needle or by some other indicator. It is only by this means that he can rapidly attain his purpose, and have full oversight of his experiments at any moment.

The *torsion galvanometer* is not only an excellent aid in determining current strength, but it can also be applied in measuring pressure. This may be accomplished by inserting resistances of varying degree. This galvanometer has an internal resistance of one ohm, and 1° of deflection represents 0.001 ampere. When pressure is to be measured, $1^\circ = 0.001 \times 1 = 0.001$ V. By the insertion of 9 Ω , the total resistance of the apparatus becomes 10 Ω ; that is, it is ten times greater than at first, and, in conse-

quence, 1° deflection corresponds to ten times its original value, which also follows from the formula of Ohm: $E = 0.001 \times 10 = 0.01$ V.

The insertion of 99Ω raises the total resistance to 100Ω , and 1° deflection corresponds to $0.001 \times 100 = 0.1$ V.

The insertion of 999Ω increases the entire resistance of the apparatus to 1000Ω , and 1° deflection corresponds to $0.001 \times 1000 = 1$ V.

For convenience, the three resistances, 9, 99, and 999Ω , are introduced into a box, and can be inserted in the circuit by means of a plug. To avoid injuring the apparatus, when ascertaining unknown pressures, it is best to throw in the greatest resistance at first, then proceed downward to the lowest. The poles should be so arranged that the magnetic needle is deflected in a direction opposite to the graduation. By turning the torsion screw in the line of graduation, the indicator is again brought back to the zero mark, and the angle of torsion may then be read. If this be too small, the torsion spring is released by turning it back to the zero mark, and a plug is inserted at the next highest point of resistance. This is repeated until the angle of deflection is sufficiently large.

The principles of construction in all amperemeters now in use permit of the application of the latter as voltmeters, hence these occur in the greatest varieties and with the greatest differences in capacity. Externally, they resemble the amperemeters, but differ

from them in having many more coils of wire and in their high resistance.

Amperemeters and voltmeters containing spirals or springs should be tested, from time to time, as to their accuracy, particularly if they are to be used continuously in a circuit.

REGULATION OF CURRENT.

The previous chapters have dealt with the production of the current and its measurement, both as to intensity and pressure. The methods by which it can be altered within any desired limits will be next considered.

It follows from Ohm's law: $I = \frac{E}{\Sigma w}$, that I can be altered in two ways: either by alteration of pressure, the total resistance remaining the same, or by changing the total resistance, the pressure remaining the same.

A. ALTERATION OF CURRENT STRENGTH BY CHANGE IN PRESSURE.

With primary or secondary batteries, the pressure may be varied by arranging a smaller or larger number in series. It has already been stated that, in the case of batteries with high resistance, the introduction of each cell into the circuit is accompanied by an appreciable change in the expression Σw .

With dynamos it is possible to alter the pressure,

without disturbing the construction of the machine, by changing the velocity or by altering the resistance in the magnet coils. An example was given on page 30, showing how, by increasing the velocity, the pressure on open circuit was increased, and mention was also made that in setting up a dynamo for experimental purposes it is well to provide it with a cone-pulley, so that the middle pulley would cause the normal velocity and the other two either a higher or a lower speed. If the variations, above or below, are maintained within 20 per cent. of the maximum or minimum, there is no danger of doing harm to the machine. This is furthermore true, because, in a machine used in an experimental plant, the requirements are not continuous, but only temporary, and for conditions that are extraordinary.

The second method of altering the pressure consists in inserting a resistance, by means of the regulating shunt, in the limb of the magnet (p. 28). This, however, merely lowers the pressure. If the regulator supplied by the manufacturer allows only a moderate reduction, it can be connected with larger resistances.

B. ALTERATION OF CURRENT STRENGTH BY ALTERATION IN TOTAL RESISTANCE.

Two distinct conditions may occur here. Increase in current strength may be achieved—

1. *By reduction of the internal resistance of the source of the current.* This refers especially to bat-

teries. Their internal resistance may be diminished by placing several of them parallel, or by the use of a larger form of the same kind of battery. This is also true of storage cells, but it must be observed that such conditions rarely obtain, because this source of current has but slight internal resistance. It can only happen should the current required for an experiment be greater than the heaviest discharge allowed for this type of battery.


The internal resistance of dynamos can not be diminished.

2. *By reduction of the external resistance.* Under this head the conducting wires must be considered. Those used in electrolytic experiments should be as short as possible and not too light in weight. For the minor experiments, good copper wires of 2 mm. diameter will be sufficient. It is customary to allow about from 2 to 3 amperes for a copper wire with a cross-section of one sq. mm.

The resistance of the experimental cell, or "bath," as it is usually termed, may be reduced—

- (1) by increasing the electrode surfaces,
 - (2) by diminishing their distance from one another,
 - (3) by increasing the conductivity of the electrolyte,
 - (4) by using a thinner or more porous diaphragm,
- if such is required by the bath.

It often happens, in using some source of electricity, —*e. g.*, a dynamo or an aggregation of storage cells,

where there is abundant pressure and but slight internal resistance,—that the current and pressure must be reduced to some definite value. This can be accomplished by throwing resistances into the circuit. German silver wires (or nickelin or rheotan), of varying diameters, arranged in spiral or zigzag form upon a frame of wood, answer well for this purpose. At suitable distances solder on short, thick copper wires, which dip into mercury cups. When such a resistance is introduced into the circuit, the current is compelled to pass through all the wire divisions; and in order that the resistance may be lowered, it is usual to throw out one or several of the divisions. This is generally done by connecting the corresponding mercury cups with a copper wire having this shape . To screw the individual wires to metal blocks, and throw out the several divisions by introducing plugs, is less worthy of recommendation, because usually the metallic blocks soon become worn and the plugs do not fit well. Furthermore, such plug contacts do not long remain bright and clean in a laboratory atmosphere. The adjustable rheostats (Fig. 13) are better. In them the individual resistance divisions are directed to metal buttons; over these passes the movable arm.

The resistances of the several divisions of wire are numbered as is done in the case of a box of weights: 1, 2, 2, 5, 10, 20, 20, 50, etc., \mathcal{Q} ; or, by doubling each

value, 1, 2, 4, 8, 16,— Ω . By the latter plan more is accomplished with the same number of resistances, but the arrangement is less convenient.

The resistance of a wire is greater, the thinner it is; hence, it might be thought that it would be more advantageous to use a very light wire, for then the

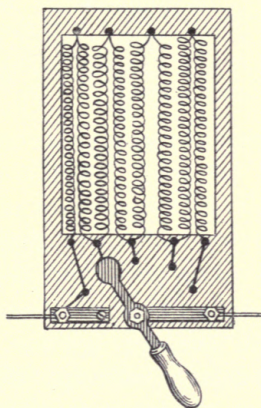


FIG. 13.

minimum quantity of wire would be consumed. This conclusion is, however, false. The electric energy annihilated by a wire is transformed into heat. On sending a current of moderate strength through a very thin wire, the increase in temperature could rise to the ignition point, or even to the point of fusion of

the wire. In making calculation for a current regulator, the intensity of the current passing through each division or section must be considered. The following table gives results obtained in experimenting with nickelin wires; it may prove of assistance in making the calculation for current regulators :

DIAMETER IN MM.	RESISTANCE FOR 1 M.LENGTH IN Ω .	IGNITION BEGINS WITH AMPERES.
0.2	13	1.7
0.4	3.2	4
0.6	1.41	7
0.8	0.79	9½
1.0	0.51	14½
1.25	0.33	20
1.50	0.23	32
1.75	0.16	40
2.0	0.13	45

The current strength given here should not be actually reached, because ignition always proves destructive to resistance wires (p. 116). With powerful currents, such as dynamos give, wires will no longer answer, because the cooling of a wire by increasing its thickness is always unfavorable. Hence, it is preferable and better to take short strips of thin sheet nickelin. These, with a section equal to that of a wire, can carry much heavier currents and yet not ignite.

STRIPS OF NICKELIN, 0.3 MM. IN THICKNESS.

WIDTH IN MM.	RESISTANCE FOR 1 M. LENGTH IN Ω .	MAXIMUM CHARGE IN AMPERES.
10	0.133	40
15	0.0889	60
20	0.0667	80
25	0.0533	95
30	0.0444	110
35	0.0381	130
40	0.0333	145
45	0.0296	160
50	0.0267	175

The maximum charges given above are so measured that the sheets of metal, under the ordinary methods of cooling, never reach the ignition point. They will not fuse through until the current is doubled or trebled. Several metal sheets can be screwed or soldered together.

B. ARRANGEMENT OF EXPERIMENTS.

THE VESSELS.

In the initial experiments, when electrolysis is to be employed, it is best, where possible, to use glass vessels, simply because the latter permit the eye to observe many of the changes occurring. For example, by transmitted light, alterations in concentration at the electrodes may be detected by the formation

of currents in the liquid; alterations in color, the intensity of the gas evolution at different points on the electrodes, the separate stages in the production of precipitates at the kathode, and the solution of the anode, as well as other points of interest, can be noted.

The general introduction of storage cells of many sizes has made it possible to obtain glass jars of the

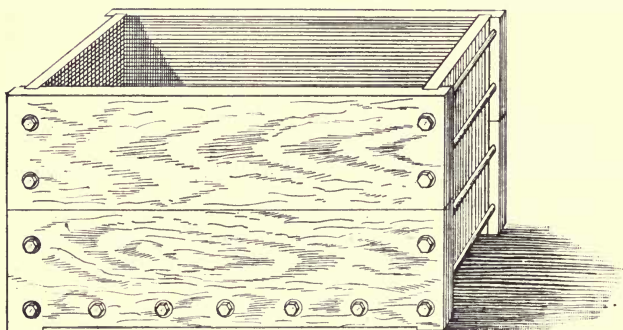


FIG. 14.

most varying dimensions. Smaller vessels may be prepared by painting cigar-boxes, etc., on the interior and exterior with paraffin. Such baths answer for both acid and alkaline liquids. They will last for several weeks at least.

With experiments conducted on a larger scale, earthenware troughs or boxes, such as are now used in galvanizing establishments, are much employed. They are, however, being gradually sup-

planted by wooden vessels lined with lead (Fig. 14). The latter are made of stout planks, provided with tongue and groove, with addition of a tarred string, and are tightly bound together and screwed up with bolts. The inner surface of these receptacles is covered with tar or pitch, or, what is better, with sheet-lead. The separate lead sheets are then welded together at their edges with an oxyhydrogen flame, so that the receptacle is really a water-tight lead box, resting in a frame of wood.

DIAPHRAGMS.

When, in an electrolytic process, substances are produced at one or at both electrodes, which prove to be soluble in water, it is impossible, unless suitable means are adopted, to prevent the separated material from mixing. Substances thus separating and again mixing destroy one another, or react upon one another in a very undesirable way. To obviate this, a porous diaphragm is introduced between the electrodes. It should, first of all, prevent the products, appearing at the electrodes, from mixing. Next, it should offer little resistance to the passage of the current, and it should, from a mechanical standpoint, be firm and durable, and not affected either by the chemicals present in the bath, or by any which may be produced in it. The material composing it should be easily obtained and inexpensive. These requirements

are fulfilled with difficulty, hence anything approximating the chief requirements must suffice. The preparation of a diaphragm, satisfactory in every particular, is still a problem of the future. Wide fields will be opened up to electrolysis when once this desideratum is found. The discovery of a diaphragm suitable for acid and also for alkaline liquids, would certainly bring a high pecuniary reward. Recently, efforts have been made to conduct, on a technical scale, operations requiring diaphragms, but without success, and the consequence has been that manufacturers have turned again to those processes and materials in which these disturbing factors (diaphragms) are not present.

Bunsen, in preparing metallic magnesium from the fused chloride, brought into notice the simplest form of diaphragm. He introduced a partition from above into the fused mass; two communicating chambers were thus formed, and into them he introduced the electrodes. Chlorine can not remain dissolved in the fused mass; it rises immediately to the surface, where it distributes itself and escapes with much foaming. The diaphragm prevents it from passing into the second chamber, where the magnesium collects in little globules.

In galvanic batteries we noticed that the porous cup acted really as a diaphragm. These cups answer well or poorly for the work for which they are constructed, depending upon the material and the temperature at

which they have been baked. A method for testing them has already been given on p. 13, and it is not necessary to repeat the same here. For acid liquids porous cups answer well enough, but they are useless with alkaline liquids, because the latter decompose and soon destroy them. When experimenting on a small scale, the porous cups are satisfactory enough as diaphragms, but in technical operations their comparatively high price, and their short life, due oftentimes to their fragility, prevent their general adoption. When the products sought are costly, the use of diaphragms is to be recommended. The cylindrical form of porous cup is usually quite inconvenient in the construction of apparatus, hence it will be found to be more practical to use plates of porous clay; these should be placed in the baths as diaphragms. The formation of such chambers as would result in this way must produce no insurmountable difficulties.

Quite frequently the sole purpose of the diaphragm is to prevent pulverulent substances separated at one electrode from passing to the other electrode. In such instances the diaphragm is really nothing more than a filter, so that a bag of silk or muslin can be attached to the respective electrode (see old form of silver voltmeter, p. 38).

The material used in technical operations, at least in an experimental way, for diaphragm purposes, has been parchment paper, felt, or asbestos.

THE ELECTRODES.

To save space, electrodes are generally in plate or sheet form. These are hung parallel in the bath. This arrangement allows the use of both sides of the electrodes. When the purpose is to throw a metal out of solution, a sheet kathode of the same metal should be used to get rid of impurities. Otherwise the choice of kathode material is merely dependent upon the nature of the liquid which it is proposed to decompose. A favorable circumstance which may be mentioned in this connection is, that the kathode is protected from corrosion under the liquid, by the reducing action of the current. In acid liquids lead or copper is employed, while iron is used in alkaline liquids. The electrodes should dip far into the liquid, first, in order that the material may be used, second, because the salts of the solution creep up and strongly corrode that portion of the electrode which is not immersed. Particular attention should be directed to the points of contact, otherwise great resistance may be introduced, and, indeed, the current can eventually be entirely interrupted. Exposed points should be protected by a layer of varnish.

Anodes, according to their deportment toward a current, are divided into two groups. The first group comprises those anodes which decompose and are dissolved—the *soluble anodes*. In the second group are the *insoluble anodes*. Soluble anodes should be used

if it can possibly be done in the process under study. The insoluble anodes are platinum, lead, and carbon for acid and neutral solutions, while iron is used in alkaline liquids.

At the ordinary temperatures platinum anodes are not attacked in solutions of any kind, not even by the halogens; hence they are the most satisfactory material for experimental purposes. Their high price prevents their general adoption in technical work. The attempt has been made to substitute platinum coated sheets for plates of the pure metal, without, however, any degree of success. The platinum coated material is not sufficiently dense and adherent to prevent the solution of the metal beneath it. With platinum anodes, the union between the plate and the wire is always effected by rivets or by welding, but not by soldering, as the gold used in soldering is not only dissolved by the halogens, but also by the oxygen acids during the electrolytic process.

Sheets of lead form very satisfactory anodes in solutions of pure sulphuric acid. They soon become coated with a brownish-black, protecting layer of lead dioxide (PbO_2), otherwise oxygen appears upon them just as it does with platinum. (The author has observed that the oxygen liberated upon a lead anode is free from ozone.) The lead dioxide slowly separates in leafy scales, which are increased by interruption of the current. The consumption of lead, however, is in no sense more appreciable. In the presence

of halogens and nitric acid, the lead is attacked more rapidly, but irregularly, with the production of white layers of chloride or sulphate (p. 87).

When there is an evolution of chlorine, the third substance, carbon, is stable, but it is strongly attacked in all cases where oxygen is evolved. Carbon anodes serve admirably in hydrochloric acid solutions, but in sulphuric acid they are visibly affected, large black scales falling off, while a brown dye-stuff dissolves. The resistance of carbon being so much greater than that of the metals, the carbon anodes must, consequently, be of much larger cross-section. The conductivity and the power of resisting the action of chemicals are greater, the harder and denser the carbon is; therefore, cut retort-carbon is better than the artificial and compressed carbon. The creeping of solutions on the porous carbon plates is disagreeable and troublesome, causing destruction of the contact points. It may be overcome by paraffining the carbons (p. 12).

Thus far no material has been discovered which will answer as a durable anode in electrolytic processes where mixtures of chlorine and oxygen are produced. Platinum is too expensive and carbon is consumed too rapidly. A process of this class—a process of eminent importance—in which this difficulty is keenly felt, is the electrolysis of sodium chloride for the manufacture of chlorine and caustic soda.

THE CONDUCTORS.

Soft copper is invariably used to conduct the current. In minor experiments, the ordinary, refined copper with a conductivity of from 52 to 56 will suffice. In technical operations, electrolytic copper is used. Its conductivity varies from 58.5 to 60. If, at any time, it is necessary to throw in a flexible piece, experiments on a small scale will require only a thin spiral, but in the larger operations a piece of copper cable will be the most suitable. The contacts must all be kept bright. When they become dull, as happens at the electrodes, it should be the care of the operator to inspect them frequently and brighten them up. The cross-section is so chosen that in conductors of moderate length, say up to 20 meters, not more than 3 amperes will fall to 1 sq. mm. It follows from this that in using powerful currents large cross-sections are requisite, and consequently that conducting rods of very considerable cost are necessary. It is best, in general, not to use currents exceeding 500 amperes. To increase the production, and yet use a single machine, it is better to increase the pressure than to increase the current strength. To conduct or distribute the current from the main line, screw clamps of the most varied construction may be used (Fig. 15).

The screw *a* is used to connect two wires; it is pushed over the one wire. *b* and *c* are very conveni-

ent modifications for the construction of apparatus. They are either screwed directly into wood (*b*), or, like the table connector *c*, are fastened to a table by means of two screws. *d* serves to connect a sheet and wire conductor. *e* is used to connect larger conducting rods. The hinge arrangement permits of its attachment from without.

Cylindrical rods are not well suited for conducting purposes, because the borings in the binding screws

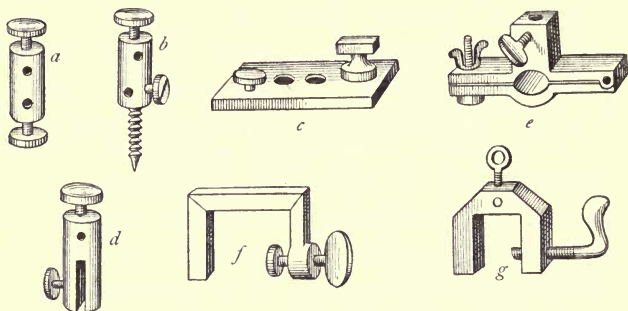


FIG. 15.

are only intended for a single wire. A much more convenient arrangement is the flat conducting wire. This can then be attached to the machine, and there being a larger contact surface, one can be assured of a more complete distribution of the current. The "rider" binding screw *f* can be clamped to this. The binding screw *g* facilitates conduction by means of the round wire.

An essential for every electric conductor is the "key" or "switch." At the completion of every experiment, the main current must be interrupted. This is necessary in order to prevent a reverse discharge of the experimental cell. In minor experiments the wires are merely withdrawn from the binding posts or screws. In larger or technical operations an adjustable rheostat is used. The contact of the latter breaks the entire current. To renew the electrolysis, the dynamo is permitted to run until it has gained its maximum speed and pressure; then the crank or arm of the switch is slowly moved over the individual resistances until the point is reached at which full current again sets in. The current and energy consumption are gradually raised to the maximum; a damaging loading of the machine, by jerks, is thus avoided; for this would happen were the full current turned on at once.

THE ELECTROLYTE.

Not much in general is to be said concerning the electrolyte. It may be either crude material to be changed by the electrolysis, and then its properties are regarded as assumed in the purchase; or, it is a means to an end—*e. g.*, the purification or refinement of metals. Then the effort is made to have its chemical properties such that they will answer for the requirements of the designed process. In the refinement of

copper, the electrolyte is the *sulphate*, because lead, antimony, tin, and gold dissolve in it with difficulty. If a chloride solution should be employed, the metals mentioned would first pass into solution, and later they would reappear in the precipitate.

The electrolyte should be as good a conductor as possible, so that little energy will be required to overcome its resistance. Conductivity increases with increasing concentration, by acidulation, and by the application of heat. A maximum conductivity is imparted to many substances by increasing their concentration. The application of heat to the electrolyte is permissible when no undesirable secondary reactions and no appreciable expense are incurred. As a rule, the liquors are sensibly heated by the current itself.

In experiments with organic substances, it may be added that they must, in all cases, be dissolved before they are subjected to electrolysis. When they are insoluble in water, they should be brought into a suitable condition for the action of the current by means of acids, alkalies, etc.

An advantage in many electrolytic processes is found in maintaining a thorough agitation of the electrolyte; this can be effected by circulation or by mechanical means. It is in electrometallurgy particularly that a more or less complete circulation of the liquor plays an important rôle.

THE ARRANGEMENT OF EXPERIMENTS.

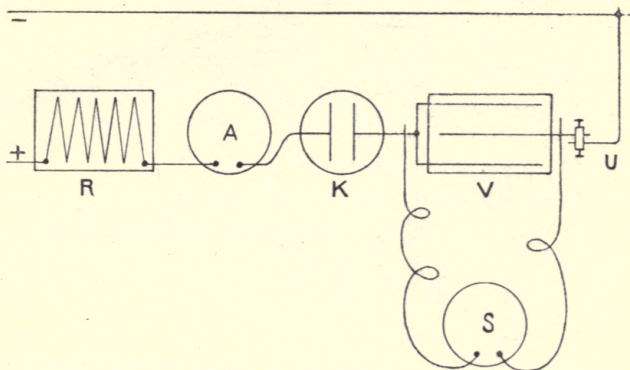


FIG. 16.

The regulating resistance R is first thrown into the circuit. It is followed by A —an apparatus intended to measure the current strength. This is either a technical amperemeter, a galvanometer, or the shunt of a galvanometer. If the experiment is to be carried out quantitatively, the ampere-hour meter is next inserted; it is the copper voltameter K . The current is then introduced and passes through the experimental cell V , the screw-clamp U , used to interrupt the current, and then back to the battery. To ascertain the pressure in the experimental cell the instrument S is attached to the two electrodes by means of a thin copper wire. This instrument is either a volt-

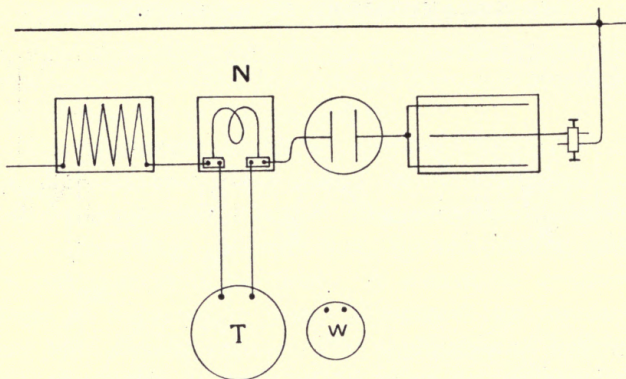


FIG. 17.

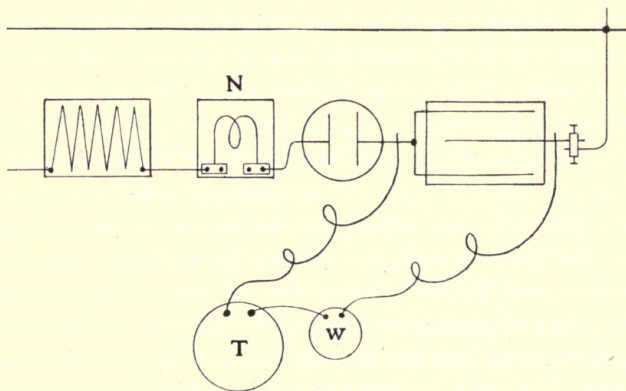


FIG. 18.

meter or a torsion galvanometer, provided with a series resistance. The latter instrument can be used both for the measurement of current and of pressure, by attaching its conducting wires to the shunt-resistance *N* or to the series resistance *W*, in connection with the experimental cell (Figs. 17 and 18).

All such aids as are used in a chemical examination of the precipitates, solutions, and gases arising in an electrolytic experiment, are to be considered as a part of the necessary outfit.

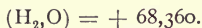
C. PHENOMENA ARISING IN ELECTROLYSIS.

PRESSURE OF DECOMPOSITION. POLARIZING CURRENTS.

When water acidified with sulphuric acid is electrolysed with insoluble anodes and a varying electromotive force, it will be observed that its decomposition begins when the pressure = 1.5 V. Water can not be resolved into its components—hydrogen and oxygen—with a lower pressure. The higher this factor rises, the more energetic will the current be. As in the case of water, so, too, in every other chemical compound, there is a certain minimum pressure, below which decomposition does not occur. When hydrogen and oxygen combine to yield water,

heat is evolved, energy is dissipated. The water molecule has less energy than its components possessed when they were free and before they united. If, then, the water molecule is to be decomposed, this will only be possible by applying an amount of energy equal to that which is lost in its formation. This energy is supplied by the electromotive force of the current. The law of the conservation of energy would lead to the hope that the decomposition-pressure might be calculated. This is, indeed, possible.

The *heat modulus* (thermal value) is the number of calories, in grams, set free in the formation of a molecule of a chemical compound referred to one gram of hydrogen as a unit. The thermal value of water is, therefore, $+ 68,360^{\circ}\text{C.}$: *i. e.*, in the union of 2 grams of hydrogen with 16 grams of oxygen, forming 18 grams of water, heat is evolved sufficient to raise 68,360 grams of water 1°C. This is expressed symbolically by placing a comma between the symbols of the several elements and enclosing the whole in brackets:



Water of solution is represented by "aq." This is always very large in proportion to the dissolved substance. (KCl aq) represents the aqueous solution of a molecule of potassium chloride.

Knowing the *thermal value* (heat modulus) attached to an electrolytic process, the decomposition-pressure

may be calculated in the following manner : * Divide the thermal value (heat modulus) W by the product of 23,067 multiplied by the number of valences dissolved by the current:

$$Z = \frac{W}{n \cdot 23,067}.$$

Examples :

1. In the case of (H_2O) :

$$\begin{aligned} W &= 68,360. \\ n &= 2, \end{aligned}$$

$$\text{therefore } Z = \frac{68,360}{2 \cdot 23,067} = 1.48 \text{ V.}$$

2. In the decomposition of copper sulphate ($CuSO_4, aq$), with insoluble anodes, into copper, oxygen, and sulphuric acid ($Cu, O, SO_3 aq$) we find

$$\begin{aligned} W &= 55,960 \\ n &= 2, \end{aligned}$$

$$\text{consequently } Z = \frac{55,960}{2 \cdot 23,067} = 1.21 \text{ V.}$$

3. In the decomposition of $(AgCl)$ into (Ag, Cl) :

$$\begin{aligned} W &= 29,380 \\ n &= 1, \end{aligned}$$

$$\text{hence } Z = 1.27 \text{ V.}$$

If the current supply in an electrolysis be interrupted and a galvanometer be connected with the electrodes, it will be observed, from the deflection,

* The deduction of this formula is given in any complete volume on Physics.

that a current proceeds from the electrodes, which, as regards direction, is the opposite of that which was originally sent through the electrodes. At first it will be quite strong, but it will gradually grow less. This phenomenon has long been known under the name of "current polarization." It is attributable or due to the ions, separated at the electrodes, seeking to re-unite to the original compound.

The current produced in this way must manifestly be opposed to the original current. If the products of electrolysis are not removed, should they remain in the solid or liquid condition in the vicinity of the two electrodes, the polarization current can, depending upon its quantity, enrich the original primary current very materially (storage cells). If gas evolution has occurred at one or both of the electrodes, the polarization current can carry only a fraction of the primary current. At first, so long as the electrodes are covered by a gaseous layer, this current is quite powerful, but it diminishes rapidly. The polarization current is also responsible for another phenomenon. If primary batteries are used in carrying on an electrolytic process,—a process well adapted from the preceding statements for the production of a continuous polarization current,—it may occur in time that the electromotive force of the elements will be exhausted and become equal to that of the polarization current. Then, equilibrium would be established between the battery and the experimental cell, with

the consequent cessation of current. If, for any reasons, the pressure of the battery continues to fall even lower, the direction of current will be reversed; the experimental cell will discharge itself, like a storage cell, into the battery. A like occurrence, discharge of the experimental cell, with annihilation of all that has already been accomplished, will be observed, if, when a dynamo is employed for the source of current, the circuit is not interrupted at the close of the work. The armature then acts like a short circuit. The polarization current can, under certain conditions, become so powerful that it will be strong enough to again set the inactive machine into motion.

The decomposition-pressure previously mentioned, is also the maximum electromotive force of the polarization current. It can usually be determined by permitting the electrolysis to proceed for some time, then interrupting the source of current and as quickly as possible attaching the torsion galvanometer. In this manner it may also be demonstrated that the electromotive force of the polarization current gradually grows less.

When *soluble metallic anodes* are employed in an electrolysis, the conditions become complicated. The anion—the constituent deposited at the anode—is not liberated as such, but combines in *statu nascenti* with the substance of the anode. This union develops heat which is favorable to the process. Consequently, the current is not called on to furnish

all the energy required: it is only necessary that this should equal the difference between the two thermal values (heat moduli), *i. e.*, the heat of decomposition of the electrolyte minus the heat of formation of the new compound produced at the anode. If the anode consists of the same metal as that which is to be deposited from a solution, *e. g.*, as in a copper or silver voltameter, then the pressure of decomposition becomes zero, for the energy consumed at the kathode in the decomposition of copper sulphate into $\text{Cu} + \text{SO}_4$ is just as great as that produced at the anode by the union of SO_4 with Cu. When the pressure of decomposition equals zero, naturally there can be no polarization current; hence it is said of such combinations that "the polarization is removed by the choice of soluble anodes." In practice, the decomposition-pressure never entirely disappears, but is only more or less reduced, hence the polarization current, arising from the reaction, may be constantly detected.

Attention may here be called to a misunderstanding which the author has frequently encountered. We read, and sometimes hear, that the polarization may be removed by blowing a current of air into the experimental cell. If a gas is developed in a process the scheme proposed can accomplish merely this, *viz.*—that after the short circuit of the cell only a very small fraction of the current first introduced reappears as polarizing current. This is because the one

product of the electrolysis—the gas—is removed, therefore the material for the prolongation of the polarizing current is absent. It is a mistake, however, to suppose that by the mere blowing-in of air it is possible to obtain a lower decomposition-pressure. The chemical reaction which the current completes, is, as has been observed, ample for this purpose, and this is in no sense influenced by blowing in air.

A second special case arises in the use of soluble anodes, consisting, not of metal, but of some chemical compound. As a typical case, the process of Marchese* may be here introduced. In it plates of copper, serving as kathodes, are hung in a solution of blue vitriol, while the anodes consist of plates made from copper-matte. The latter is mainly cuprous sulphide (Cu_2S), with a small amount of iron sulphide (FeS). The following reactions occur: Copper, from the blue vitriol solution, separates at the kathode. It has the thermal value ($\text{Cu}, \text{SO}_4 \text{ aq}$). Sulphur appears at the anode, while copper dissolves as sulphate— CuSO_4 . The course of the reaction may be imagined to progress in this way: At first the copper sulphide breaks down into sulphur and copper; and for this change a quantity of energy corresponding to the thermal value (Cu_2S) will be requisite. After this the liberated copper will be converted into copper sulphate, and in so doing

* D. R.-P., Nr. 22429.

produces energy corresponding to the thermal value ($\text{Cu}, \text{SO}_4 \text{ aq}$). Since the thermal value of the electrolysis is equal to the algebraic sum of the thermal values developed at the two electrodes, we then have, if the heat consumption be represented by $-$, and the heat production by $+$,



The first and third members fall away, so that in the process the actual energy-quantity is that corresponding to the decomposition of the copper sulphide. As (Cu_2S) equals 20,270 c, the decomposition-pressure will be

$$Z = \frac{20,270}{2 \cdot 23067} = 0.44 \text{ V.}$$

This diminution in the pressure of decomposition only occurs when the material to be dissolved is a conductor of electricity and serves, at the same time, as anode, so that the solution occurs in consequence of the direct action of the current. For example, this end would not be attained if insoluble anodes were used, and the ore were to be suspended in the bath by means of baskets. A solution of the ore occurring in this way, if indeed it did happen, would be a secondary reaction, which would have absolutely nothing to do with the electrolysis, hence would not affect the required pressure.

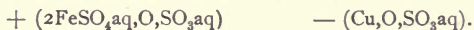
Recently several suggestions have been made for obtaining metals electrolytically which seek to reduce

the pressure of decomposition by a very peculiar method. Thus, insoluble anodes have been used and these are hung in the solution of some readily oxidizable substance. The electrodes are, therefore, separated from one another by a diaphragm. Indeed, Siemens (D. R.-P., 42243 and 48959) electrolyzed a mixed solution of ferrous sulphate and copper sulphate by allowing the solution first to pass through the kathode chamber, and then through the anode compartment. In this way copper was deposited at the kathode, after which the solution of ferrous sulphate passed to the anode where it took up the atomic group SO_4 —the anion separated from the copper sulphate—and became ferric sulphate. The latter was next digested with finely divided chalcoppyrite or copper-matte. Sulphur separated, the ferric salt was reduced, and copper sulphide dissolved, thus regenerating the original liquid, which in turn was again subjected to electrolysis.

The thermochemical changes were :



The thermal values needed here are not exactly known. The difference in question can, however, be calculated by writing the reactions differently :



The heat of oxidation resulting from the conversion of ferrous into ferric sulphate may be ascertained

by subtracting the heat of formation of two molecules of ferrous sulphate from the thermal value (heat modulus) of ferric sulphate :

$$\begin{array}{r}
 (\text{Fe}_2\text{O}_3, 3\text{SO}_3\text{aq}) = 224,880 \text{ c.} \\
 - 2(\text{FeO}, \text{SO}_3\text{aq}) = - 186,400 \text{ c.} \\
 \hline
 (2\text{FeSO}_4\text{aq}, \text{O}, \text{SO}_3\text{aq}) = 38,480 \text{ c.}
 \end{array}$$

Hence the heat consumption at the kathode ($\text{Cu}, \text{O}, -\text{SO}_3\text{aq}$) equals 55,960, the heat produced at the anode 38480, and the difference would be 17,480 c, which would correspond to a pressure of 0.38 V.

In fact, the author, experimenting on a small scale and observing the precautions laid down on p. 80, was able to confirm a pressure of decomposition equal to 0.38–0.41 V. by using platinum anodes, and on substituting anodes of carbon found 0.37–0.40 V. A sheet of lead, used as anode, gave an evolution of oxygen and a decomposition pressure of 1.26 V. This also occurred when the experiments were varied in every possible way. Therefore Siemens' process is only practicable with platinum or carbon anodes, but not with lead anodes! There is no explanation of this rather singular deportment.

Höpfner (D. R-P., 53782), using cuprous chloride, and Seegall (D. R-P., 53196) employing ferrous chloride, pursued an idea similar to that of Siemens. The suggestion that oxidizable salts should be used in electrolysis is deserving of great consideration.

As observed in the Siemens process, the nature of

the electrodes also exercises an influence upon the pressure. An example will show this. When a copper sulphate solution is electrolyzed with platinum anodes the pressure of decomposition will be observed to be 1.26 V. On substituting lead anodes these will gradually become coated with dioxide (PbO_2) and on making a test, the pressure of decomposition will be found to be 1.55–1.60 V. This is due to the reactions which give rise to the polarization current. The reverse electrolysis takes place with platinum anodes, while with lead anodes there comes into play the formation of lead sulphate (PbSO_4) from the oxide (PbO) and the sulphuric acid (H_2SO_4). The dioxide at the anode first loses an atom of oxygen and passes into oxide (PbO), which unites with the free sulphuric acid to form lead sulphate and water. In fact, the heat, resulting from the formation of the lead dioxide (PbO_2) from lead (Pb) and oxygen (O_2) should tend to diminish the pressure of the primary electrolysis; yet nothing of this kind is observed, because the main reaction evolves oxygen, and but little of it is consumed in the formation of PbO_2 . With the polarizing current, however, the gradually accumulating dioxide immediately comes into evidence with its entire mass.

The magnitude of the pressure of decomposition and its eventual diminution by means of aid-reactions, are of the greatest importance for the commercial success of a process or method. In the case of a

metallic conductor the pressure E , which is necessary to preserve a current of I ampere in a resistance w , equals:

$$E = I. w.$$

In the electrolysis there is added to this the pressure of decomposition Z , so that for every electrolysis the necessary pressure is

$$E = I. w + Z.$$

In this expression Z is a constant, determined only by the nature of the electrolytic process and wholly independent of the dimensions of the bath. The value $I. w$., however, is most intimately connected with the dimensions of the bath and is smaller, the lower the resistance w of the bath. Consequently Z is usually greater than $I. w$. and will, in large measure, determine the pressure necessary for carrying on the work of the bath. The higher the pressure, however, the greater will the energy consumption for a definite production be. *Hence, in every electrolytic process, care must be exercised to have the pressure of decomposition as low as possible, i. e., use soluble anodes whenever it is possible, or if this be not practicable, endeavor to facilitate the electrolytic process by other aid-reactions.*

FARADAY'S LAW. CURRENT EFFICIENCY.

When a current is passed through different solutions in series, the products separated in equal peri-

ods of time are in proportion to their equivalent weights—(law of Faraday).

For example, the same current in an equal period of time, decomposes

1 molecule of HCl, AgNO₃, KOH ;

$\frac{1}{2}$ “ “ ZnCl₂, CuSO₄, H₂O ;

$\frac{1}{3}$ “ “ AuCl₃, NH₃, etc.

As a current of one ampere precipitates 4.02 grams of silver per hour, it is easy to calculate the number of grams of any substance which will be decomposed or deposited in a definite period of time.

Example. How much blue vitriol can be decomposed daily, in a bath, using a current of 50 amperes? How much copper will be deposited?

In accordance with the law just stated above, for every atom, or 107.6 parts by weight of silver, one-half molecule = 124.6 parts of CuSO₄.5H₂O will be decomposed, and consequently $\frac{1}{2}$ Cu = 31.6 parts by weight of copper will be deposited. One ampere-hour corresponds to 4.02 grams of silver,

hence $4.02 \cdot \frac{124.6}{107.6} = 4.65$ grams of blue vitriol and

$4.02 \cdot \frac{31.6}{107.6} = 1.18$ grams of copper; so that in

24 hours, with a current of 50 amperes: $24 \cdot 50 \cdot 4.65 = 5580$ grams of CuSO₄.5 aq will be decomposed and there will separate $24 \cdot 50 \cdot 1.18 = 1416$ grams of copper.

When a metal enters its compounds with varying

valence, the quantities of that metal deposited by the current will naturally vary according to the valence. With the same current, Cu_2Cl_2 will yield twice as much copper as CuSO_4 . In most instances the reductions first proceed to the lowest state of oxidation before the metal begins to separate.

Very few electrolytic processes proceed in a simple way. In most cases secondary reactions play an important rôle. There is a double possibility for this: unintentional oxidations can occur at the anode or reductions at the kathode. In such instances the law of Faraday serves for the sum of the reactions occasioned by the current. In the decomposition of copper nitrate, metallic copper appears at the kathode, while a portion of the nitric acid is reduced to lower oxides of nitrogen, or even to ammonia. Oxygen is liberated at the anode, and is partially consumed in the reoxidation to nitric acid of the nitrogen oxides formed at the kathode. When ferric chloride is electrolyzed, ferrous chloride and metallic iron occur at the kathode, which is, in turn, converted at the anode into ferric chloride. A similar phenomenon explains why manganese can not be quantitatively precipitated at the anode from a liquid containing iron, because the salts, in a lower state of oxidation, which have been simultaneously formed, favor the re-resolution of portions of the manganese.

It is of the utmost importance to know the quantitative course of an electrolytic process. That por-

tion of the total current sent into a bath, which is active in the direction desired, represents the *current efficiency*, while the remainder, consumed in undesired secondary reactions, is the *current loss*. In every electrolytic process the secondary reactions should be determined both qualitatively and quantitatively, and by alteration of conditions the effort should be made to eliminate these disturbing factors. The character of the side reactions may be discovered by a qualitative examination of the electrolyte after the completion of the experiment, and the amount of loss by a direct determination of the current yield (efficiency).

To this end insert an ampere-hour meter (a copper voltameter) in the circuit in series with the experimental cell (see p. 52). Fill a large beaker or glass jar with copper sulphate (p. 40), observing the arrangement of apparatus and the size of the kathode, as indicated on p. 53. When the experiment is finished, determine the increase in weight of the kathode, and by Faraday's law calculate how much of the desired product should be present in the experimental cell. The actual amount is learned by weighing, or by titration, and its percentage may then be calculated.

Example. In the electrolysis of a solution of salt, after a certain time, 650 c.c. of liquor, containing 4 per cent. NaOH, were obtained. During this same period 30.4 grams of copper had been deposited in

the copper voltameter. Calculate the *current yield* (efficiency).

According to Faraday's law, 2 molecules, or 80 parts by weight of caustic soda, result for each atom, or 63.2 parts by weight of copper; hence, for the 30.4 grams of copper obtained in the experiment, 38.5 grams of NaOH would be produced ($63.2 : 80 = 30.4 : x = 38.48$). The actual yield was

$$650 \cdot \frac{4}{100} = 26.0 \text{ grams.}$$

Hence the current efficiency would be

$$\frac{26}{38.5} = 67.5 \text{ per cent.}$$

The rest of the current, equaling 32.5 per cent., was therefore expended upon other reactions.

ION TRANSFERENCE.

In electrolysis the components of a compound are not only liberated from their molecular union, but they undergo a rearrangement. If the movement of the liquid particles is not interfered with, this phenomenon will not be noticed, but if it is restricted by a diaphragm, alterations in concentration will be observed at the electrodes.

This interesting phenomenon, which can not be considered theoretically at this time, may be best understood by an example. Decompose dilute sul-

phuric acid (56.7 grams acid to the liter) between two semicylindrical sheets of lead, by a current of one ampere. Electrolytic gas will be set free, and at the expiration of the experiment the acid will show the same concentration which it first had. A porous cup is next introduced between the electrodes. In three hours the acid in the cup will contain 63.25 grams of sulphuric acid per liter, while the external liquid will contain 55.47 grams per liter of the same acid. After two additional hours the contents will be found to be 68.77 grams and 52.86 grams respectively. Hence a transference has occurred on the part of the sulphuric acid, toward the anode; and it has been withdrawn from the vicinity of the kathode. By reversing the experiment, it will be observed that this phenomenon is independent of the varying sizes of the electrode surfaces. On mixing the two portions of acid there will result an acid containing 57.1 grams per liter. Its slight difference from the original content is due to the acid of unknown concentration absorbed by the porous cup. Next, take the smaller sheet of lead, which has been hung in the porous cup, and let it serve as kathode while the larger is made the anode. In three hours the concentration will be as follows:

in the porous cup (—)	50.65	grams	H_2SO_4	per	liter
outside the porous cup (+)	60.04	“	“	“	“

Again, the acid in the anode chamber has been enriched. Similar phenomena invariably show them-

selves if diaphragms are used in the work. They must be considered as a part of the investigation because they influence the concentration of the liquors either favorably or unfavorably.

CURRENT DENSITY.

The quantity of the products formed in any electrolytic process accords with the law of Faraday and the current strength; the quality, however, as well as the nature of the reactions, depends in many instances chiefly upon the size of the electrode surfaces. *Current density* is the current strength for a *unit* of surface of an electrode. In technical operations the unit of surface is the *sq. m.*, but in scientific researches it is ordinarily the *sq. dm.* Whether a metal is deposited electrolytically in a spongy, crystalline, or amorphous form depends very much upon the current density prevailing at the kathode. The smaller the electrode surface the more energetically must the action of the current show itself. Thus, Bunsen, by using exceedingly high current densities, actually succeeded in precipitating metallic chromium from an aqueous solution.

In working with soluble anodes, the influence of current density will also find expression. When the current density is low, the individual constituents of the anode will dissolve one after the other. Metals in solution will be precipitated one after the other, in

accordance with the law that the metal which develops the greatest energy in its solution will first dissolve, and that one which for its deposition requires the consumption of the least quantity of energy will be first precipitated. As the density increases, these reactions take place almost simultaneously. From a neutral solution containing copper and zinc, a current of low density will first throw out the copper, while with higher density an alloy of copper and zinc, *i. e.*, brass, will be deposited.

In an electrolytic process in which metals are not precipitated, but where gases or substances soluble in water are separated, it might be assumed that the current density was of no moment. This, however, is not the case. If there is a possibility of producing different stages in the oxidations or reductions occurring at the electrodes, as, for example, is often the case with organic bodies, the higher density will always produce a more far-reaching oxidation or reduction than the current with low density.

In addition to the physical character and the chemical nature of the depositions which are formed, the current density further exercises an influence on the pressure of the bath. If, in arranging for an experiment, the size and distance of the electrodes from one another, as well as the nature of the electrolyte, remain unchanged and the current density alone be varied, it will be observed that the bath pressure will increase simultaneously with the density of the cur-

rent. This phenomenon is not singular or strange because, inasmuch as the resistance of the bath is not altered, a higher current-strength can, according to Ohm's law, only be attained by a higher pressure.

THE WORKING PRESSURE.

Although the dependence of the pressure upon various circumstances has been touched upon at many points in the preceding chapter, these relations must again be considered from a common point of view.

The working pressure depends:

(1) Upon the decomposition-pressure developed by the thermal value of the process under consideration.

(2) Upon the sum of all the resistances of the bath.

(3) Upon the current density which must be maintained.

Economy demands that the working pressure shall be low. Let us see how this can be accomplished.

(a) The decomposition-pressure of a process is dependent upon the chemical changes producing it: hence it can not be changed at will. However, as indicated upon p. 82, it is possible in many instances to bring in a reaction which will aid the electrolysis—one which will produce heat—and thereby diminish the consumption of external energy—in the form of electricity. The use of soluble anodes and the

continuous addition of oxidizable substances to insoluble anodes may also be mentioned in this connection.

(*b*) The resistance of the bath may be reduced by greater concentration of solution, the addition of a free acid, if this is advisable or allowable, by heating the electrolyte, and by bringing the electrodes nearer together. In arranging the electrodes care should be exercised that short-circuiting between adjacent electrodes is not only avoided but is impossible. The resistance in a liquid can be diminished not only by bringing the electrodes nearer together, but also by increasing their surface, because thereby the liquid layer to be traversed by the current will acquire a larger cross-section. This is, however, scarcely allowable because the size of the electrode surfaces has already been fixed by the current density most favorable for the operation. A slight advantage can be obtained by having the electrodes of unequal size. The occasion will be rare when the current density at *both* electrodes must have a definite value. This is necessary usually for only one electrode, either the negative or positive, depending upon the nature of the process. Therefore, the other electrode may be made larger, and in this way the resistance in the liquid will be diminished. It is only possible to make an essential gain in this manner when the two electrodes show decided differences in size.

(*c*) When the density and composition of the so-

lution in an electrolytic process are given, the pressure value is at once fixed and only the minor details can now be considered, such as may be produced by a greater or less distance between the electrodes and a higher or lower bath temperature. With such provisions the pressure can no longer be varied at will without changing both the current density and the separation of the electrodes. With unchanged solution and unchanged distances between the electrodes, there is of necessity a lower density for a lower pressure, and *vice versa*.

D. THE PRELIMINARY EXPERIMENTS NECESSARY FOR AN ELECTRO- CHEMICAL PROCESS.

If electricity is to be used in carrying out a process, answers should be given to the following questions:

1. What are the most favorable conditions for the experiment?
2. What expense will attend the process?

The experiment should not be conducted on too contracted a scale. The selected electrodes should have 100 sq. cm. surface per side. This is particularly desirable where metal precipitations are concerned. The metallic deposits on the edges of the electrodes are generally different from those appearing on the middle of its surface, so that a false judgment might

easily follow if the electrode had, so to speak, only an edge surface.

As electrolyte choose a solution apparently suitable for the purpose, and at first vary the current density. Note the pressures which are produced, and observe the physical and chemical nature of the deposits; examine the secondary reactions both qualitatively and quantitatively. Next alter the composition of the solution—let it be more dilute, more concentrated, neutral, acid, alkaline. Change the salts until a suitable solution and proper current density have been found. When the most favorable conditions have been discovered, make a few preliminary experiments upon the current efficiency, and when it is possible let this be done with extremes in temperature (high and low) which are likely to figure in the practical application. During the course of the experiment it will no doubt become patent that the construction of the apparatus must be altered. In all such changes consider the question: Will this arrangement prove satisfactory if the dimensions are those required when working on a large scale? Technical experiments should not be performed with apparatus whose principles can not be applied practically. Results obtained with such apparatus have little, if any, technical value, simply because they can not be directly introduced into practice.

In the whole course of the experiments such frequent opportunity is offered to exercise the ingenuity

as chemist, physicist, and engineer, that it is unnecessary to speak of all the possible conditions.

When the most favorable experimental conditions have been found and suitable apparatus has been constructed, advance is made to the next stage of the experiment by having a small dynamo act for several weeks or months on a number of baths arranged in series. A more extended view of the process is thus gained, and the deficiencies in construction appear which in the case of smaller apparatus would be overlooked. When the faults have been largely removed and the plant works well, a calculation for larger conditions can be undertaken without fear of stumbling upon great deceptions or mistakes.

E. CALCULATION OF THE NECESSARY POWER. CHOICE OF DYNAMOS.

To calculate the power required for an electrochemical process it is necessary to know the pressure and current efficiency for each bath.

Suppose that the bath pressure equals s volts, and the current yield σ per cent., then the work of a horsepower would be

1 HP = $\frac{V \times \text{amperes}}{736}$; with a pressure, therefore, of s volts there would consequently result $\frac{736}{s}$ amperes

to the horse-power. If a grams of some definite substance is produced per ampere-hour (see Table 1), then for each horse-power hour there would result $\frac{736}{s}$ a grams. Since the current efficiency is never quantitative, but only equal to σ per cent., the value above must be further multiplied by $\frac{\sigma}{100}$ and then it becomes $\frac{736 \cdot a \cdot \sigma}{s \cdot 100}$. Finally, a correction must be added for the efficiency ν of the dynamo. In the case of small dynamos $\nu = 75$ to 80 per cent., whereas with larger machines and normal loads this value rises to 93 per cent.

Hence the actual yield for each horse-power hour is $\frac{736 \cdot a \cdot \sigma \cdot \nu}{s \cdot 100 \cdot 100}$ grams; or introducing the limiting values of ν —75 per cent. to 93 per cent.—given above, the production p for a horse-power hour becomes, depending upon the size of the machine used—

$$p = \frac{552}{s} \cdot a \cdot \frac{\sigma}{100} \text{ to } \frac{684}{s} \cdot a \cdot \frac{\sigma}{100}.$$

Having thus deduced the production for a horse-power hour, the daily production, having a definite power at command, can easily be ascertained, or the reverse, viz., the power requisite to manufacture daily 100 kg. of any product.

In projecting a plant, the result above indicated will not be sufficient. Regard must also be had

to the mixing and transportation of the liquor, to the working of the adjunct machinery, etc. If a steam boiler is necessary, attention must be paid to the consumption of steam in heating the liquor, and at least to the heating of the working-rooms by steam during the winter.

As regards the choice of dynamos, it may be said that, so far as its efficiency goes, it is immaterial whether medium pressure and powerful current or high pressure and low current be employed. However, the following must be observed: If the nature of the process in any manner permits, *i. e.*, if the baths are alike and regularly served, they should be arranged in series. The number thus introduced into the circuit, and the pressure that the machine will consequently have, will depend upon whether frequent disturbances occur, due to cleansing of the baths or electrodes, fresh charges, etc. In electrolytic copper refining, 40 to 50 baths are arranged in series, but with a less active plant 15 to 20 constitute a very respectable number. If each bath requires a pressure of s volts and if n baths of this kind are to be used in series, a pressure of $V = n \cdot s$ volts will be required of the dynamo. As a rule, the pressure of the machine should be higher than that calculated, because by constant work it falls in consequence of the heating of the armature, and also because of imperfect contacts here and there. The latter can scarcely be avoided, so that an increased pressure

is necessary to maintain an undiminished current strength. When the entire electromotive force of the dynamo is not needed, the excess is cut off by being sent through a shunt regulator.

A reserve dynamo should always be on hand, so that in case of repairs to the running machine the action of the current need not be interrupted for days or weeks. It is recommended to use the one machine for day work, and the other for work at night. In this way both machines are better protected than if they be run until some part or parts are completely used up. By an arrangement such as the preceding, the periods required for cleaning can also be minimized, and the person in charge, finally, can have a better oversight of the dynamos. Each workman can then supervise his own machine, and can not conceal any mistakes which may have occurred in its operation. Again, it will be easy in this way to arouse the sense of honor of each attendant so that he will strive to keep his machine in the best condition.

In addition to the expense incurred in obtaining the power it is necessary, when calculating the cost of the manufacture, to include* interest on the purchase sums for the entire plant (buildings, machinery, instruments, baths, conductors), the cost of chemicals con-

* See also Berg- u. Hüttenmänn. Zeitung, 1893, 52.

sumed in the process, and wages, as well as loss in interest due to the storage of the necessary supplies of crude material.

F. PRACTICAL PART.

1. CONSTRUCTION AND CALIBRATION OF A TANGENT GALVANOMETER.

A very simple contrivance shown in the accompanying Fig. 19, and answering every purpose, may

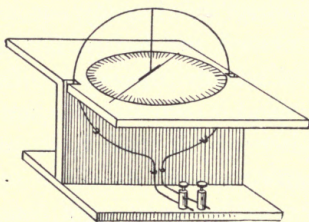


FIG. 19.

be made by any experimenter. It requires no special description. Notches are made in the little table at the points where the wire passes through it. It must, however, have margin enough to support a glass cover, intended to protect the needle from air-currents. The needle is a short magnetic steel rod (a knitting needle). That the angle of deflection on

the largely divided circle may be conveniently read, attach to the needle by means of shellac or wax a thin hollow glass thread filled with ink. A fiber of the finest sewing silk will answer for the suspension filament. This also is placed upon the sealing wax, and by momentary contact with a hot wire is attached to the needle. A drop of wax or paraffin brought upon the glass tube will serve to balance the needle. This device, it is true, is very primitive, but it will suffice for many purposes, especially when it is only intended to obtain an approximate idea of the current strength, or whether it changes during the experiment.

Tangent galvanometers are calibrated by bringing them into circuit with a voltmeter (arrangement of experiment: battery—galvanometer—voltmeter—battery) and observing the deflections α_1 and α_2 , with varying current strengths, I and I_2 . According to p. 44:

$$I = c \cdot \text{tang. } \alpha,$$

consequently

$$c = \frac{I}{\text{tang. } \alpha}.$$

The values for c , deduced from the two experiments, must agree fairly well. Determine their mean and calculate a table for the different deflections.

EXAMPLE. The length of the needle is 28 mm., and the diameter of the circle is 167 mm.

Experiment 1. In six minutes 0.0508 gram of metallic copper was obtained in the copper voltmeter ;

the deflection in the galvanometer averaged 12° . The precipitation of copper per hour would, therefore, be 0.508 gram, and as 1.181 grams copper, per hour, correspond to 1 ampere, the calculated current strength would be $\frac{0.508}{1.181} = 0.430$ ampere. The constants of the galvanometer may, therefore, be calculated from the equation—

$$c = \frac{0.430}{\text{tang. } 12^\circ} = 2.023.$$

Experiment 2. In six minutes 0.0963 gram of copper was precipitated. The average deflection was 22° . Therefore the current strength was

$$I = \frac{0.963}{1.181} = 0.815 \text{ ampere,}$$

hence

$$c = \frac{0.815}{\text{tang. } 22^\circ} = 2.017.$$

hence

The mean of the two experiments is $c = 2.02$. This is, at the same time, the current strength for the deflection-angle 45° ($\text{tang. } 45^\circ = 1$). A table for the galvanometer can now be constructed:

1° deflection :	I = 2.02 tang. 1° = 0.035 Amp.,
2° “	I = 2.02 tang. 2° = 0.070 “
3° “	I = 2.02 tang. 3° = 0.106 “
	etc.

2. CALIBRATION OF A GALVANOMETER BY MEANS OF A SHUNT.

If it is desired to enlarge the capacity of this very sensitive instrument, recourse may be had to a shunt. This must be considered and arranged as a part of the main circuit. As all sensitive galvanometers have a great number of turns, and as these are usually wound flat, the constants can not be established by one or two experiments, but must be determined empirically. This is done by making a number of readings with different current strengths, the results being then transferred to millimeter paper on which the current strengths appear as the abscissas and the corresponding deflections as the ordinates. The points fixed in this manner are then united into a continuous curve, from which, by inverting the order, current strengths corresponding to all deflections can be obtained.

The lower the resistance of the shunt, the stronger may the currents be for which the instrument is available. It should be remembered that in consequence of the sensitiveness of the apparatus the needle may be appreciably influenced by the main current if the galvanometer be set up in too close proximity to the latter. Whenever possible, place the galvanometer from $\frac{3}{4}$ to 1 m. from the main current. Should the galvanometer always occupy the same position, the disturbance may be disregarded, because it has

been fully allowed for in the curve previously constructed. If, however, the galvanometer and its shunt are to be used in different localities, it is quite necessary to remove them from the main current to the distance mentioned.

When a delicate galvanometer can not be had, a very simple form can be constructed after the style of the tangent instrument described in the preceding chap-

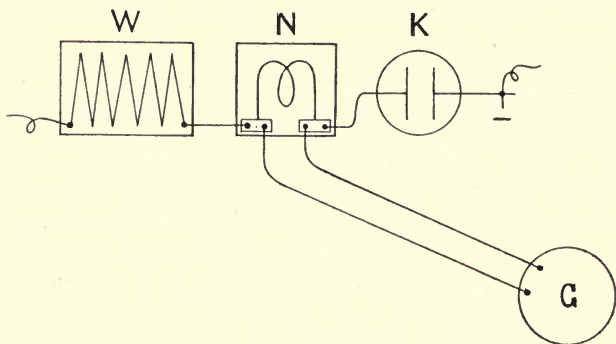


FIG. 20.

ter. Instead of the single copper ring, use a coil of covered copper wire having numerous turns. The needle may be large in proportion to the diameter of the ring, as no use will be made of the tangent law.

Example. A delicate instrument provided with a bell magnet and copper damping was used as the galvanometer (Hartmann and Braun, Frankfort-on-the-

Main); its resistance was 3.35Ω . The shunt consisted of 1 m. of copper wire 2 mm. in diameter, at each end of which a plate of metal with two clamps was attached by solder. This shunt N, a copper voltameter K, and a resistance W, serving to vary the current strength, were arranged in series in the same circuit. The galvanometer G, was connected with the shunt N by means of two copper wires, 1 m. in length (Fig. 20). (These two connecting wires form a part of the branch resistance, hence, in subsequent measurements, can not be exchanged for any other two wires.)

Produce with W currents of different strengths; note the deflection, and weigh the copper deposited in a unit of time (6 minutes, preferably, as they equal $\frac{1}{10}$ of an hour).

DURATION OF EXPERIMENT. MINUTES.	DEFLECTION. DEG.	PRECIPITATED COPPER IN GRAMS.	CURRENT STRENGTH. AMPERES.
6	5.6	0.0114	0.096
6	7.5	0.0154	0.130
6	10.8	0.0222	0.187
6	14.3	0.0307	0.259
8	20.0	0.0599	0.379
6	22.1	0.0502	0.423
7	24.5	0.0661	0.478
6	28.0	0.0668	0.563
6	32.0	0.0802	0.676
6	37.0	0.0961	0.810
6	43.0	0.1200	1.012
6	49.0	0.1488	1.255

In Fig. 21 the preceding current strengths appear as abscissas, the corresponding deflections as ordinates, and the resulting points of intersection indicated by crosses form the connecting curve :

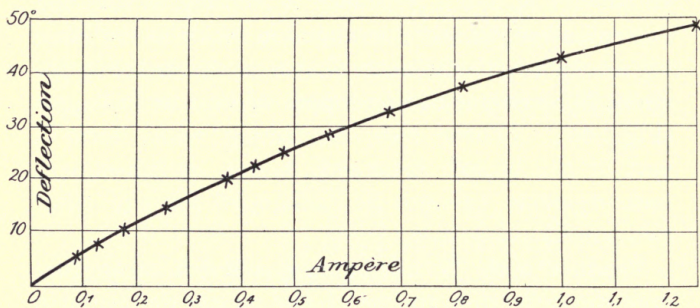


FIG. 21.

The following table can be read from this curve as a result of the calibration :

AMPERES.	DEFLECTIONS.
0.1	6 °
0.2	11.5
0.3	16.3
0.4	21.0
0.5	25.
0.6	29.
0.7	33.
0.8	36.5
0.9	39.5
1.0	43.0
1.1	46.
1.2	48.
1.25	49.

3. CONSTRUCTION OF AN INSTRUMENT TO MEASURE PRESSURE.

If several storage cells are at the disposal of the operator, the galvanometer used in the preceding experiment may be calibrated so as to measure pressure. When a single accumulator has lost a small part of its charge, its pressure may be accepted as fairly accurate if taken as 2.0 V. If the cell be discharged by a German silver wire, the resistance of which has been so chosen that the wire never becomes too hot and the current allowed for the cell is never exceeded, there will exist between the terminals of the German silver wire a pressure of two volts; at the middle it will have one volt, and between the one terminal and the first quarter 0.5 volt, etc. If a wire 1 m. in length has been selected, each cm. of it will correspond to $\frac{1}{10}$ of the pressure prevailing at the terminals. Hence it will only be necessary to successively connect the galvanometer by its wires to the points of the German silver wire representing 0.1, 0.2, 0.3, etc., V. pressure, and note the deflections in order to use the instrument as a voltmeter graduated in tenths. In order to obtain suitable deflections of the galvanometer it must be provided with a series resistance the size of which will depend upon the pressure and the delicacy of the instrument. As mentioned on p. 54, the use of a high series resistance increases or en-

larges the applicability of the instrument. Hence, having the choice between a less delicate galvanometer with lower series resistance, and one that is very delicate, and for the introduction of which a high resistance will be necessary, it will be wise to choose the latter.

Example. A piece of fine German silver wire, 2 m. in length, is stretched over a narrow board, which at its terminals is soldered to binding screws, connected by stout copper wires to two accumulators, in series, having a maximum discharge capacity of ten amperes. As the resistance of the wire equals 6.67Ω , there exists in it, during the experiment, a current strength of $\frac{4}{6.67} = 0.6$ ampere. To obtain a proper angle of deflection for the pressure of 4.0 V. prevailing at the terminals use a series resistance of about 550Ω . Under the stretched wire is placed a scale 2 meters in length and divided into 40 equal parts. The division lines are five cm. apart and the pressures are written at these points. The calibration from $\frac{1}{10}$ to $\frac{1}{10}$ V. is made in such a manner that the one binding screw of the galvanometer is connected by a fine wire to the first binding screw of the German silver wire, while the other binding screw with the inserted resistance W is connected with a long, flexible wire. This is carried along the German silver wire and at each division the corresponding deflection of the galvanometer noted. Fig. 22 represents the arrangement as projected.

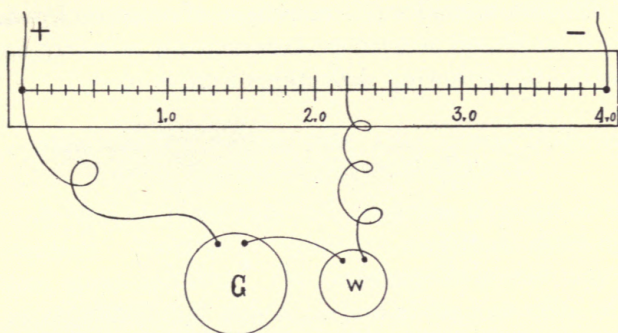


FIG. 22.

The values obtained when $W = \text{about } 550 \text{ } \Omega$ are:

PRESSURES.	DEFLECTIONS.
0.1 V.	2.1°
0.2	4.5
0.3	6.6
0.4	8.7
0.5	10.8
0.6	12.8
0.7	14.6
.	.
.	.
.	.
3.6	51.6
3.7	52.3
3.8	53.0
3.9	53.7
4.0	54.4

When a second series resistance of only 100 Ω was used to obtain a greater accuracy for a lower capacity, the following deflections were observed :

PRESSURES.	DEFLECTIONS.
0.10 V.	12°
0.15	17.2
0.20	22.5
0.25	27.4
0.30	31.7
.	.
.	.
.	.
0.80	56.5
0.85	58.1
0.90	59.4
0.95	60.7
1.00	61.8

The pressure corresponding to each degree of the galvanometer may be ascertained by carefully constructing a curve, as shown on p. 110, from the observations made and then taking from it the numbers not directly observed.

Series resistances may be constructed by winding covered nickelin or rheotan wires,* of 0.2 mm. diameter, upon wooden spools.

Each wire has an approximate resistance of 15 Ω per meter. Stout copper wires should be soldered to the terminals and the whole apparatus be then placed

* May be obtained from F. A. Lange, Berlin C., Seydelstrasse.



in a box or under a glass cover, the terminals of the copper wire alone projecting beyond the latter.

4. THE CALCULATION FOR AND CONSTRUCTION OF A REGULATING RESISTANCE.

A battery of storage cells is at the disposal of the chemist. Each cell is allowed a maximum discharge rate of ten amperes. The resistance in circuit may be so regulated that only a portion of the four cells need be connected for pressure. This, however, would be a crude arrangement, and, furthermore, the cells would be discharged unequally, so that after the lapse of a certain period some of the cells would be exhausted, while others would still be in a workable condition. It would be best, if possible, to utilize all the cells in every experiment. They would then sustain equal discharge, and could subsequently be equally charged. A wire is therefore run from the battery to the experiment table. Somewhere in the line introduce a regulator, which will enable the operator to reduce the current in every possible way and without making any great jumps. When several experiments are to be conducted simultaneously by means of the same battery, throw in such a resistance between each individual experiment and the main circuit. The resistance wires are of such a size that the passing currents are not sufficient to ignite them. The wires should not be too long and not too different in kind.

The ordinary arrangement of the battery is such that the four cells are placed in series. Their yield would then be 8 V. and 10 amperes. The group arrangement of 2×2 cells with a yield of 20 amperes and 4 V. rarely occurs. The maximum current strength, due to the resistance in question is, therefore, 20 amperes. Disregarding altogether the resistance in the experiment under consideration, the 20 amperes appear with a resistance of $\frac{4}{20} = 0.2 \Omega$ and 10 amperes flow in a circuit where the resistance is $\frac{8}{10} = 0.8 \Omega$. The wire for the resistance subdivisions under 1Ω should be so selected that it may safely carry 20 amperes. From the table on p. 63 nickelin wire 1.5 mm. in diameter would answer. If it is desired to regulate down to 0.2 ampere, a total resistance of $\frac{8}{0.2} = 40 \Omega$ would be requisite. Indeed, with 40Ω it is possible to get even below this point, because the resistance of the conducting wires in the particular experiment must always be added, and its decomposition-pressure must be deducted from the 8 or 4 V. of the battery.

Selecting the subdivisions 0.25, 0.25, 0.5, 1, 2, 2, 5, 10, 20Ω , the corresponding current strengths in the separate subdivisions, and the diameter of the nickelin wire, suitable for the same, may be found as follows:

SUBDIVISION.	CURRENT STRENGTH.	DIAMETER OF WIRE.
Up to 1 Ω	20—10 amperes	1.5 mm.
2—5 “	4—1.6 “	0.7 “
10—40 “	0.8—0.2 “	0.3 “


The entire regulating resistance then arranges itself as follows :

SUBDIVISION.	LENGTH AND SIZE OF NICKELIN WIRE.	
0.25 Ω	1.09 m.	1.5 mm.
0.25 “	1.09 “	
0.5 “	2.17 “	
1. “	0.96 “	0.7 “
2. “	1.92 “	
2. “	1.92 “	
5. “	0.89 “	0.3 “
10. “	1.79 “	
20. “	3.57 “	

The first of these wires is arranged in a long loop, provided with a sliding contact, so that its resistance can be changed from 0. to 0.25 Ω by mere alteration in position. Two thin copper plates, bound together, answer for the sliding contact. They are pushed over the wire loop as indicated in Fig. 23, *a*. The remaining wires are wound in spirals and attached to a frame, each of their ends being soldered *

* Every person engaging in electrolytic experiments should possess some skill in soldering. Contacts which are to act well for long periods are best prepared by soldering. The bright, clean terminals of the two wires are wrapped about each other, moistened with a solution of zinc chloride, heated in the flame of a Bunsen or alcohol lamp, and the heated point touched with a thin hammered piece of tin, until the latter melts and flows smoothly over the soldered spot. If the solder does not spread, the wires are again moistened with “solder-water,”

to a piece of stout copper wire which dips into a cup of mercury.

To throw out a resistance subdivision, unite the corresponding mercury cups with a copper wire having this form .

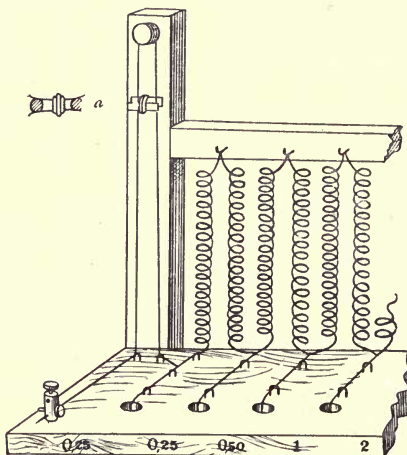


FIG. 23.

5. WORKING A COPPER LIQUOR CONTAINING ARSENIC.

Problem. A factory produces daily 5 cb. m. of liquor, which contains 40 grams of copper as sulphate

and the manipulation repeated. With practice the end may soon be attained with ease. Each solder-point must be washed to remove any adherent acid, which would gradually destroy the metal.

and 10 grams of arsenic as arsenic acid, per liter. Other heavy metals are present only in small quantity, while chlorine and nitric acid are absent. The attempt is to be made to purify the copper as far as possible in the electrolytic way, and to separate it in a marketable form. Make an estimate of the probable cost of the plant with the necessary power, keeping in view its future expansion.

It is a fact well known to every chemist that copper can not be separated quantitatively, as metal, in the electrolytic way from solutions containing arsenic without some of the latter being carried down with it. At the beginning of the electrolysis pure copper, bright red in color, separates; but it gradually grows paler, and in a comparatively short time it is steel gray, or even black, from the co-precipitated arsenic. The bright blue color of the solution, at this point, is evidence that the liquid is not yet free from copper.

In the electrolytic separation of two bodies, such as are presented in this case, two considerations must be observed: the proper *current density* and the *agitation* of the liquor. When the current density is high, the velocity with which chemical reactions must occur at every point of the kathode will leave very little time for the current to select from among the separate bodies in the solution, so that two or even more of them will be simultaneously precipitated. With low current density, however, the possibility of such a

selection will occur. Hence a very definite relation between the copper and arsenic content of a solution exists for every current density beyond which point the copper precipitated will contain arsenic. These limits should be determined.

The liquid at the kathode, from which copper has been deposited, becomes specifically lighter and rises to the surface. This upward movement of liquid at the kathode can be readily shown by carrying out the experiment in a glass vessel and examining the solution by transmitted light. The liquid rising in the vicinity of the kathode becomes, in consequence of the diminished copper content, relatively richer in arsenic, as compared with the major portion of the solution. Unfavorable mixture conditions, therefore, exist about the kathode unless the difference is destroyed by constant stirring. Thorough agitation of the liquor becomes necessary in proportion as the kathode plates are longer.

With the preceding observations before us, the course of the investigation is clearly indicated. To obtain as much pure copper as possible, the liquor must be constantly agitated. It must also be determined, with varying current densities, at what copper-content of the liquor the experiment should be interrupted to prevent the deposition of arsenic. The current efficiency and the bath pressure should be ascertained by an inserted voltameter. The last two factors form a basis for the calculation of the requisite power, while

the most favorable current density determines the necessary size of plant.

Execution of Experiments. Two paraffined cigar boxes will answer for containing vessels. They should be 11 cm. in depth and in length and be 6 cm. wide. The one contains the solution to experiment upon, while the other does service as a copper voltameter (see p. 40). The electrodes of the experimental cell consist of two plates of lead as anodes, between which is suspended a thin plate of copper, serving as kathode. Each metal plate is 10×10 cm. The electrodes of the voltameter should be a thick and a thin plate of copper of equal size. Agitate the solution by a stirrer which constantly moves two glass rods back and forth between the electrodes (30 revolutions per minute). A horizontal, not vertical, movement is preferable, because in actual practice the former is cheaper. With an up-and-down movement the weight of the agitator must be raised with each lifting; this means a considerable consumption of energy. With a to-and-fro movement of the agitator, however, a rake can be attached to a bar passing over firmly attached carrying-rolls. This does away with the weight of the agitator, and the work required for stirring, occasioned by the resistance of the liquid and the friction of the carrying rolls, is reduced to a minimum.

The current from two storage cells is made to flow through a regulating resistance, and afterward passes, in regular succession, the shunt of a galvanometer,

the experimental cell, the copper voltameter, and then back to the battery. The liquor contained 39.29 grams of copper and 9.9849 grams of arsenic per liter. The experimental cell contained 530 c.cm., corresponding to 20.822 grams of copper and 5.291 grams of arsenic.

The first experiment was conducted with a current $I = 1.257$ amperes (calculated from the voltameter), the kathode surface immersed in the liquor was 10×8.4 cm., hence the surface used was 168 sq. cm., and the current density was $D = \frac{1.257}{1.68} = 0.748$ ampere for each sq. dm. In trade, whole numbers are preferred; hence, in calculating the current density, the square meter, one hundred times as great, is taken as the unit. The current density in the preceding case would then be "75 amperes per sq. m." The pressure remained nearly constant at 1.92 V.

The experiment was interrupted at the close of eight and one-half hours. The precipitated copper had a perfectly bright color, and weighed 12.109 grams. In the voltameter 12.613 grams of copper were deposited, consequently the current efficiency was

$$\frac{12.109}{12.613} = 96 \text{ per cent.}$$

After two additional hours the plate of metal in the voltameter had increased 2.8925 grams in weight, while the sheet in the experimental bath had in-

creased 2.820 grams. Hence the current efficiency was 97.49 per cent., the mean current strength 1.224 amperes, and the current density 73 amperes per sq. m. The precipitate was perfectly satisfactory in every respect.

The following morning the experiment was continued for two hours more. The pressure equaled 1.95 V. In the voltameter 2.8195 grams of copper had been deposited, and in the experimental bath the quantity of copper equaled 2.7828 grams. The current strength, therefore, was 1.194 amperes, the current density 71 amperes, and the current efficiency 98.7 per cent.

As the copper now began to take on an earthy color, it was assumed that the limit for the current density, so frequently mentioned, had been attained. The copper precipitated in all was

12.109 grams.
2.820 “
2.783 “
<hr/>
Total, 17.712 “

hence, there still remained in solution $20.822 - 17.712 = 3.11$ grams of copper and 5.29 grams of arsenic, or, as these quantities were dissolved in 530 c.c. of liquor, the latter contained, per liter, 5.87 grams of copper plus 9.98 grams of arsenic—*i. e.*, in round numbers, 6 grams of copper for 10 grams of arsenic.

Again, a new plate of copper was suspended in the solution. The experiment was then continued with a more feeble current, consequently with a lower current density. At the expiration of two hours there was an evident gray-colored deposit of arsenic. The observations were as follows :

The copper deposited in the voltameter was 1.4485 grams.

The copper deposited in the experimental cell was 1.3974 grams.

Pressure equaled 1.85 V.

The current strength, deduced from these data, equaled 0.613 ampere; the current density equaled 36.5 amperes per sq. m., and the current efficiency was 96.47 per cent. The liquor still contained $3.11 - 1.40 = 1.71$ grams of copper, together with 5.29 grams of arsenic, or in every liter there remained 3.23 grams of copper plus 10 grams of arsenic.

The gray-coated metallic plate was now replaced by another, and the current was still further diminished to 0.25 ampere for a kathode surface of 144 sq. cm. The current density, calculated from this, equaled 18 amperes per sq. m. The pressure was 1.69 V. After three hours the copper precipitate was still a beautiful red in color. The deposited quantities were 0.9089 gram and 0.8354 gram, from which the current efficiency of 92 per cent. was calculated.

At the end of another hour and seven minutes the copper became coated with a gray deposit of arsenic,

so that the experiment was now definitely interrupted. The solution contained 2 grams of copper and 10 grams of arsenic per liter.

These results can be best understood from the following tabular statement:

CURRENT DENSITY PER SQ. METER.	PRESSURE.	CURRENT EFFICIENCY.	THE FINAL LIQUOR.
71 Amp.	1.95 V.	97 %	6 g. Cu + 10 g. As per L.
36 “	1.85 “	96 %	3.2 g. “ “ “ “ “ “
18 “	1.69 “	92 %	2 g. “ “ “ “ “ “

It may be again mentioned that these numbers relate to liquors which were well agitated during the electrolysis.

Assuming that the preceding results have been confirmed by several controls, steps can then be taken for the calculation of the plant. The lower the current density selected, the more completely can the liquor be freed of copper. The current density of 18 amperes, tested last, is certainly not to be recommended. It gave only 4 grams more of copper than the current density 71, but to do this it required an electrode surface four times as large, hence a larger plant, and the efficiency also was about 5 per cent. less. The middle current density, that of 36 amperes, is more favorable. This, or in round numbers 40 amperes, may be made the basis of the following calculation, taking the pressure as 1.9 V. and the final liquor as containing 4 grams of copper per liter. According to these conditions, the liquor at first con-

tains 40 grams of copper per liter, and is to be worked down to 4 grams of copper per liter, hence for each liter or each cubic meter there should be obtained 36 grams or 36 kg. of copper respectively. The working of the daily production of 5 cb. m. should then yield 180 kg. of copper per day. Since the current efficiency is 96 per cent., there would be deposited for each ampere hour, not the theoretical 1.181 grams, but only $1.181 \times \frac{96}{100} = 1.133$ grams of copper. Consequently, the precipitation of 180 kg. of copper would require a quantity of electricity equal to $\frac{180,000}{1.133} = 158870$ ampere hours. As the electrolysis demands a pressure of 1.9 V., therefore the work would be $158,870 \times 1.9 = 301,853$ volt-ampere hours. This calculated into horse-power hours is $\frac{301,853}{736} = 410.1$ H. P. hours. If twenty-four hours are to be worked per day, the machine must have $\frac{410.1}{24} = 17.1$ H. P. The efficiency of a 17 horse-power dynamo can be considered equal to about 90 per cent., so that eventually the power required for the work will be found equal to $\frac{17.1}{0.90} = 19.0$ H. P.

In calculating the size of dynamo necessary for the above purpose, it may be assumed that there is a daily consumption of 301,853 volt-ampere hours.

This would require in 24 hours a steady output of $\frac{301,853}{24} = 12,577$ V. amperes. As 1 bath requires 1.9 V., the work projected could be done with a machine of 1.9 V. and 6620 amperes (as $1.9 \times 6620 = 12578$). Two baths, in series, would require $2 \times 1.9 = 3.8$ V., and $\frac{12577}{3.8} = 3310$ amperes. Four baths, with similar arrangement, would demand: pressure = 4.19 = 7.6 V., and current strength: $\frac{12577}{7.6} = 1655$ amperes, etc.

The greater the number of baths arranged in series, the greater must the pressure of the machine be, but the current strength can be correspondingly low. The current strengths mentioned above are too high for a machine. It is better, as already mentioned on p. 72, not to exceed 500 amperes. In using a current of 300 amperes the corresponding pressure would be $\frac{12577}{300} = 41.9$ V., and with this pressure it would be possible to arrange $\frac{41.9}{1.9} = 22$ baths in series. With this relatively simple working of baths twenty-two will not be too many, and the current strength will not be too high, therefore a machine of the model 42 V. AND 300 AMP. can be selected for the work. It is always well to allow a certain latitude in such matters; therefore it is best to consider propositions for a machine which, with the lowest velocity possible, will yield a

current of 300 amperes with a pressure of 42-45 V., but it must still be possible to increase it, without danger, to 350 amperes.

After the energy consumption for the process has been calculated as 19 H. P. and the dimensions of the machine are of such proportions as to give 42 V. and 300 amperes, the size of plant can be next considered—*i. e.*, the number and size of baths and the number and size of electrodes. The number of baths to be arranged in series is $\frac{42}{1.9} = 22$. As the current density must equal 40 amperes per sq. m. there should be $\frac{300}{40} = 7.5$ sq. m. of electrode surface in each bath. A suitable and convenient size for the electrodes is 50 × 50 cm. As both sides of the electrodes are used, the surface becomes 0.5 sq. m. Therefore, to get 7.5 sq. m. surface for each bath it will be necessary to use $\frac{7.5}{0.5} = 15$ such plates. The lead plates, serving as anodes, are of equal size; in number they are 16, or 1 more than the kathode strips, this is because an anode should be suspended opposite the reverse side of the last kathode plate. The lead plates should be about 2 mm. thick and the copper plates 0.3 mm. in thickness. It will be necessary to purchase the copper plates only in the initial experiment, because as the work progresses these will be produced in the process. If the kathode surfaces be covered with an exceed-

ingly thin layer of fat, a little thicker on the edges, they soon become coated with layers of copper, which can readily be removed in sheet form.

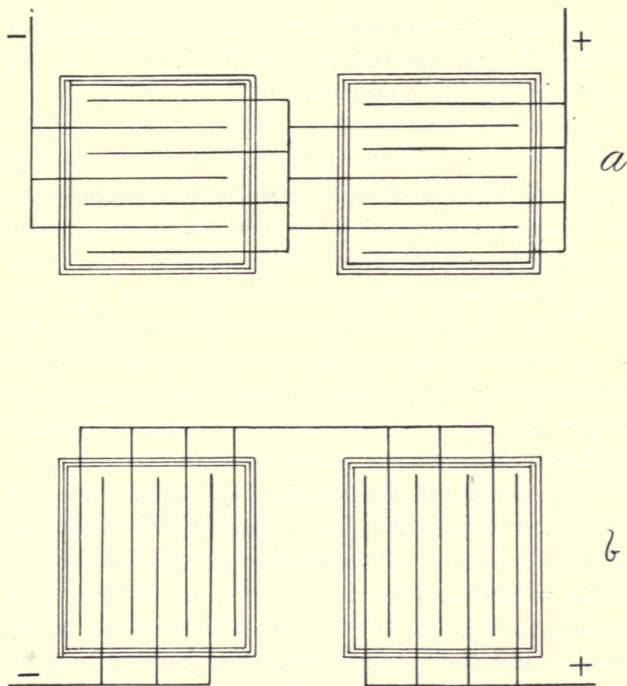


FIG. 24.

The electrodes are hung parallel in the bath, with alternating anodes and kathodes, the copper plates being connected with one another, and the plates of

lead in like manner. The current is carried to the adjacent bath by the device *a* or *b*, Fig. 24.

Directions as to the manner of fastening the electrodes, etc., will not be here given. They can be found in the various volumes of *Berg- u. Hüttenmännischen Zeitung*, as well as in Balling's *Grundriss der Electrometallurgie*, Stuttgart, 1888.

Dimensions of the Bath. In the preliminary experiments the electrodes were removed 3 cm. from each other. This separation is somewhat too small. It would be better to make the distance between them from 4 to 5 cm., so that by the buckling of the electrodes beneath the liquid surface short circuits may not arise. It is especially at the beginning of the experiment, when the copper sheets are still thin, that this danger exists. Later, when they have become thicker and firmer, it is less to be feared. When an agitator is used, it may diminish short circuiting, but in spite of this the separation of the electrodes 3 cm. from each other can still be made the basis of calculation. Thirty-one electrodes give 30 intermediate places = 90 cm., and the distance of each terminal electrode from the side of the trough being 4 cm., there would in all be a full length of 98 cm. The full width of the trough, granting equal separation of electrodes, would be $4 + 50 + 4 = 58$ cm. To prevent the lead peroxide, which slowly disintegrates, from becoming incorporated with the copper plate, the latter should not be allowed to reach entirely to the

bottom of the vessel. Its distance from the bottom should be 4 cm. Further, the trough must never be filled to overflowing. A space of 7 cm. should exist between the edge and the liquid surface. The depth, consequently, of the trough would then be $4 + 50 + 7 = 61$ cm., and the depth of liquor in it would be 54 cm. The full size of trough should, therefore, be in length, breadth, and depth $98 \times 56 \times 61$ cm. The volume of liquor would then be $9.8 \times 5.8 \times 5.4 = 307$ liters. The volume of the electrodes would cause a reduction of 10 L., leaving in all 297 liters.

Should the dimensions of the bath, using the preceding calculation as basis, prove too large, it can be divided into two, or several, smaller baths. These should be arranged parallel, and the group that results can then be introduced, in series, as one single, large bath.

An interesting question is, In what time will the contents of the bath be exhausted? As 300 amperes are active in the bath and 1.133 grams of copper are precipitated with the observed current efficiency of 96 per cent. per ampere hour, there would result an hourly yield, from the bath, of $300 \times 1.133 = 340$ grams of copper. A liter of liquor would yield $40 - 4 = 36$ grams of copper, while the contents of the trough, containing 297 L., would give, consequently, $36 \times 297 = 10,692$ grams of copper. The time requisite for this would be $\frac{10,692}{340} = 31\frac{1}{2}$ hours. At the end of this

period the entire 22 troughs would have to be replenished. This would require $22 \times 297 = 6534$ liters of liquor. During this period there have also been produced $5 \times \frac{31.5}{24} = 6.563$ cb.m. of liquor. The calculation, therefore, agrees. The working of the liquor keeps pace with its production during the operation, but care should be had for a receptacle, in which can be collected the liquors obtained from two days' operation.

The example may be amplified by calculating the daily production of the plant on the basis that copper is precipitated in 22 baths arranged in series, and that the dynamo yields 300 amperes with 42 V. Such are the statements which generally reach the public, while the actual process is held as secret. Let us see how, from such statements, the daily production, at least, can be calculated. The pressure need not be taken into account in this calculation; it is sufficient for the energy consumption. The current strength and the number of baths arranged in series, are, however, important. With 22 baths thus arranged and a current strength of 300 amperes, 300 amperes would be active in each of these baths, or a total of $22 \times 300 = 6600$. It is quite immaterial whether the 22 baths are simple, or whether 22 groups of 2, 3, or 4 baths each, in series, are worked. The only difference being that with 22 simple baths 300 amperes fall upon a single bath, whereas with 22

quadruple baths 300 amperes will fall to one quadruple bath,—a group,—so that a single bath will take $\frac{300}{4} = 75$ amperes. But in the entire circuit there will be a total of $22 \times 300 = 6600$ amperes doing actual work. For each ampere hour there is a theoretical production of 1.181 grams of copper, while the entire plant would yield, consequently, $22 \times 300 \times 1.181$ per hour, and $22 \times 300 \times 1.181 \times 24$ daily, which equals 187,070 grams of copper. This number must yet be multiplied by the current efficiency. In the preceding example it was known to be 96 per cent., so that the daily production would be $179,587 = 179\frac{1}{2}$ kg.

Instead of attempting to free the liquor from copper in a single operation, it may be worked up in two stages, at first with greater current density, reducing this toward the end, or the attempt may be made to arrange the process for continuous work. This can be effected by letting the liquor slowly enter the first bath, then conducting it into the next, and so on until it flows from the last bath fully deprived of its copper. The first baths, containing rich liquors, may have, under certain conditions, greater current densities, consequently less electrode surface than the end baths. These statements merely aim to show the possibility of reaching the desired goal by various methods.

The few grams of copper per liter, remaining in

the final liquors, are removed by hydrogen sulphide, by cementation, or by any other good method.

The evolution of oxygen during the electrolysis causes a disagreeable spattering of the liquor. This may be much diminished by swimming a sheet of oiled paper on the bath. Agitation of the liquor is then out of the question, but it can be mixed by circulation or by similar means.

6. ARRANGEMENT FOR ELECTROCHEMICAL ANALYSIS.

As a rule, the pressure needed in analyses by electrolysis does not exceed 4 V., therefore, we may use, as sources of electric energy, either 4 large Daniell cells, arranged in series, or a thermopile (largest model with 4 V.), or two secondary batteries arranged in series. The decided advantage of electrochemical analysis, its extreme accuracy, as well as the circumstance that the work in the main is self-acting, leaving the chemist free to perform other tasks, are recognized on all sides. As a consequence, electrolysis is pushing its way more and more into technical establishments. In these places many analyses are conducted simultaneously, hence the source of the energy must yield a rather powerful current and still have low internal resistance. The three arrangements previously described render this possible. Meidinger cells are not well adapted for the work, as

they have great internal resistance. The writer, using a battery consisting of 4 large Daniell cells (22 cm. high), conducted simultaneously 5 copper determinations, or two nickel estimations, and with two secondary batteries made simultaneously 12 electrolytic determinations of the most varied character. To render each electrolysis independent of the rest, as far as regards current strength, it is only necessary to insert between each experiment and the main current a suitable regulating resistance. This is most simply made as follows (Fig. 25): Two conducting strips, in the form of flat wire, are run from the battery, on the wall, along the experiment table. One of the two electrode stands is connected directly with one of the metallic conducting strips, while between the other conducting strip and the second stand-support a resistance wire is inserted (see p. 117 and Fig. 23). The brass clip, serving as a movable contact, is held firmly by pushing a short piece of rubber over it. The author uses for this purpose 1.5 m. of rheotan wire, 0.4 mm. in thickness, which represents 5.5 Ω . If, occasionally, greater resistance is necessary, connect the stands by the conducting metal strips, not with copper wire, but by means of a spiral of German silver. By pushing the movable contact back and forth the current strength can be sufficiently regulated. It may be determined by inserting, during the experiment, a measuring instrument between one of the stands and the main current. The amperemeter of

Kohlrausch * (Fig. 11) answers admirably for this purpose.

The customary electrodes are of platinum. A few

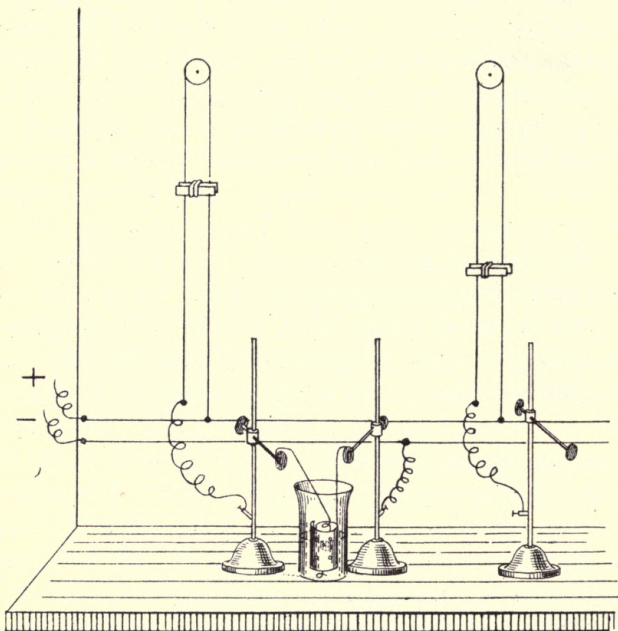


FIG. 25.

words may be mentioned in regard to their form. The electrodes, originally proposed by Luckow and

* Compare Classen, *Quantitative Analyse durch Electrolyse*. 3te Auflage, S. 52; also Smith, *Electrochemical Analysis*, second edition.

later introduced into the Mansfield works, consisted of a closed cylinder or cone. This was used as kathode, while the anode was a platinum wire. Alex. Classen, who has rendered marked service in the extension of electrolysis, particularly recommends (*loc. cit.*) platinum dishes.

The writer does not favor this idea, because the dish allows of no other interruption of the analysis than to siphon out the liquid contained in it, water being poured in at the same time to replace that which was removed. If the liquid remaining from the electrolysis is to be still used in the determination of other metals, nothing further remains than to again concentrate the diluted liquid to a suitable volume. In scientific work this is not a very disturbing factor, but in practical operations, where the question of "time" represents an expensive factor, the plan can not be adopted. By using cylindrical or cone-shaped electrodes the siphoning can easily be avoided. The electrodes should have side slits and should not be suspended from below in the stands, but from above (Fig. 26).

When the analysis is finished, loosen the screw with the left hand, pressing the electrode with the right to the stand. Raise it vertically, taking care not to touch the anode spiral. The moment the edge of the beaker glass is passed, the little liquid adhering to the edge is removed and the electrode quickly immersed in a glass containing water. The

anode is then immediately removed. It is washed with water from a wash bottle. The electrodes after washing with water are dipped into alcohol and dried directly over a flame. This procedure will perhaps cause a slight loss in liquid, but it is so slight that in technical operations it need not be at all considered. The loss equals about 0.5–0.8 c.cm.; consequently, with a residual liquid of 150 c.cm. it would be 0.3–0.5 per

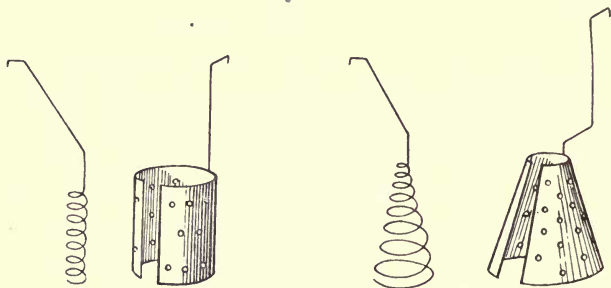


FIG. 26.

cent. of the remaining metals. For example, in the case of a sample of German silver containing 20 per cent. Ni, the error would be $\frac{20}{100} \cdot \frac{0.3}{100} = 0.06$ per cent. Ni. In contrast with this slight inaccuracy, falling within the limit of error of other methods, we have the saving of time, which is very appreciable and of importance.

The platinum cylinders and cones should have a number of perforations, so that the lines of force

arising at the central anode can exert themselves on the outer surface of the kathode. If this is neglected, the major portion of the precipitate will be found on the inner kathode surface, especially when there is not much liquid between the electrodes and the glass vessel. Since much depends, in the separation of some metals, on the current density, perforation of the kathode surface is to be recommended, so that little difference will exist between the current density upon the inner and outer surface. A wire is usually made to serve as the anode. It is bent in the most various forms. Any one in practice who would bend the anode into fantastic shapes would justly arouse astonishment. In scientific laboratories this is apparently a matter of no moment, because we find it to be almost universally the case that the bending of the anode rarely accords with the kathode. The two electrodes should be equidistant at all points, therefore a cylindrical anode is by far the most satisfactory when using a cylinder. When a cone is used, the bent wire should have the form of a cone-shaped screw (Fig. 26). The anode wires should always stand or rest on the bottom of the beaker glass, because the gas evolved about them will then effect the mixing of the solution; consequently, the lower liquid layer would stagnate did not the anode extend to the bottom of the beaker. The forms of electrodes just described and the manner of work just mentioned, have been used and followed by the writer for years,

and in several thousand electrolytic determinations have answered excellently. They fulfill all practical demands.

In communicating an electrolytic method for the determination or separation of metals, the nature of the solution, the approximate concentration, but especially the *current density* should be mentioned. Cylindrical or conical electrodes must be considered with *both* surfaces. If there be references with the reverse statement in literature, then introduce an amperemeter between the electrolytic stand and the main current, and by means of the resistance-strip, or with a rheostat, produce the current strength which has been calculated from the given current density and the size of the electrodes in use. In this way alone is it possible to use the observations of others, without necessitating a minute copying of the details of the first author. Having once ascertained for a new process how much resistance must be thrown in with the arrangements at hand, in order to arrive at the prescribed current density, it will not be absolutely necessary, in later trials, to insert the amperemeter in the circuit. It will suffice to use the resistance of the amperemeter as found.

G. TABLES.

I.

ELEMENT.	SYMBOL AND VALENCE.	ATOMIC MASS.	QUANTITY DE- POSITED PER AMPERE HOUR.
Aluminium,	Al'''	27.04	0.337 gram
Antimony,	Sb'''	119.6	1.491 "
Arsenic,	As'''	74.9	0.934 "
Barium,	Ba''	136.86	2.559 "
Bismuth,	Bi'''	207.5	2.587 "
Bromine,	Br'	79.76	2.983 "
Cadmium,	Cd''	111.70	2.088 "
Calcium,	Ca''	39.91	0.746 "
Chlorine,	Cl'	35.37	1.323 "
Chromium,	Cr'''	52.45	0.654 "
Cobalt,	Co''	58.6	1.096 "
Copper,	Cu''	63.18	1.181 "
	Cu'		2.363 "
Fluorine,	Fl'	19.06	0.713 "
Gold,	Au'''	196.2	2.446 "
Hydrogen,	H'	1	0.0374 "
Iodine,	I'	126.54	4.732 "
Iron,	Fe''	55.88	1.045 "
Lead,	Pb''	206.39	3.859 "
Lithium,	Li'	7.01	0.262 "
Magnesium,	Mg''	23.94	0.448 "
Manganese,	Mn''	54.8	1.025 "
Mercury,	Hg''	199.8	3.736 "
	Hg'		7.472 "
Nickel,	Ni''	58.6	1.096 "
Nitrogen,	N'''	14.01	0.175 "
Oxygen,	O''	15.96	0.298 "
Platinum,	Pt ^{iv}	194.34	1.817 "
Potassium,	K'	39.03	1.459 "
Silver,	Ag'	107.66	4.026 "
Sodium,	Na'	23.00	0.860 "
Strontium,	Sr''	87.30	1.632 "
Sulphur,	S''	31.98	0.598 "
Tin,	Sn''	117.35	2.194 "
Zinc,	Zn''	64.88	1.213 "

II. THERMOCHEMICAL DATA.

(From Naumann's Thermochemie.)

HYDROGEN.		ARSENIC.	
(H ₂ , O)	68360	(As ₂ , O ₃)	154590
CHLORINE.		(As ₂ , O ₃ , aq)	147040
(Cl, H)	22000	(As ₂ , O ₅)	219400
(Cl, H, aq)	39320	(As ₂ , O ₅ , aq)	225400
(Cl ₂ , O ₅ , aq)	— 20480	POTASSIUM.	
SULPHUR.		(K, O, H)	104000
(S, O ₂)	71070	(K, O, H, aq)	116460
(S, O ₂ , aq)	78770	(K, S, H, aq)	65100
(SO ₂ , O)	32160	(K ₂ , O, aq)	164560
(SO ₂ , O, aq)	71330	(K, Cl)	105610
(SO ₂ , aq, O)	63630	(K, Cl, aq)	101170
(S, O ₃)	103230	(K ₂ , O, SO ₃ aq)	195850
(SO ₃ , aq)	39170	SODIUM.	
(S, O ₄ , H ₂)	192910	(Na, O, H)	102030
(S, O ₄ , H ₂ , aq)	210760	(Na, O, H, aq)	111810
(S, H ₂)	4510	(Na, S, H, aq)	60450
(S, H ₂ , aq)	9260	(Na ₂ , O, aq)	155260
IODINE.		(Na ₂ , O, SO ₃ aq)	186640
(H, I)	— 6040	(Na, O, Cl, aq)	83310
(H, I, aq)	+ 13170	(Na, Cl)	97690
BROMINE.		(Na, Cl, aq)	96510
(Br, H)	8440	CALCIUM.	
(Br, H, aq)	28380	(Ca, O)	131360
NITROGEN.		(Ca, O, aq)	149460
(N, H ₃)	11890	(Ca, Cl ₂)	170230
(N, H ₃ , aq)	20330	(Ca, Cl ₂ , aq)	187640
(N ₂ , O)	— 18320	STRONTIUM.	
(N, O)	— 21575	(Sr, O)	130980
(N ₂ , O ₃ , aq)	— 6820	(Sr, O, aq)	157780
(N, O ₂)	— 2005	(Sr, Cl ₂)	184550
(N ₂ , O ₅ , aq)	29820	(Sr, Cl ₂ , aq)	195690
(N, O ₃ , H)	41510	BARIUM.	
(N, O ₃ , H, aq)	49090	(Ba, O)	130380
PHOSPHORUS.		(Ba, O, aq)	158260
(P, O ₄ , H ₃ , aq)	305290	(Ba, Cl ₂)	194250
		(Ba, Cl ₂ , aq)	196320

MAGNESIUM.

(Mg, O)	145860
(Mg, O, H ₂ O)	148960
(Mg, O ₂ , H ₂)	217320
(Mg, Cl ₂)	151010
(Mg, Cl ₂ , aq)	186930
(Mg, O, SO ₃ aq)	180180

ALUMINIUM.

(Al ₂ , Cl ₆)	321870
(Al ₂ , Cl ₆ , aq)	475560
(Al ₂ , O ₃ , 3SO ₃ aq)	451770

MANGANESE.

(Mn, Cl ₂)	111990
(Mn, Cl ₂ , aq)	128000
(Mn, O, H ₂ O)	94770
(Mn, O ₂ , H ₂ O)	116280
(Mn, O, SO ₃ aq)	121250

ZINC.

(Zn, O)	85430
(Zn, O, H ₂ O)	82680
(Zn, Cl ₂)	97210
(Zn, Cl ₂ , aq)	112840
(Zn, O, SO ₃ aq)	106090
(Zn, S)	41989

NICKEL.

(Ni, O, H ₂ O)	60840
(Ni, Cl ₂)	74530
(Ni, Cl ₂ , aq)	93700
(Ni, O, SO ₃ aq)	86950

COBALT.

(Co, O, H ₂ O)	63400
(Co, Cl ₂)	76480
(Co, Cl ₂ , aq)	94820
(Co, O, SO ₃ aq)	88070

IRON.

(Fe, Cl ₂)	82050
(Fe, Cl ₂ , aq)	99950
(Fe ₂ , Cl ₆)	192060
(Fe ₂ , Cl ₆ , aq)	255420
(2Fe, Cl ₂ aq, Cl ₂)	55520
(Fe, O, SO ₃ aq)	93200
(Fe ₂ , O ₃ , 3SO ₃ aq)	224880
(Fe, S)	35504

LEAD.

(Pb, O)	50300
(Pb, Cl ₂)	82770
(Pb, Cl ₂ , aq)	75970
(Pb, O, SO ₃ aq)	73800
(Pb, O, N ₂ O ₅ aq)	68070
(Pb, S)	20400

COPPER.

(Cu ₂ , O)	40810
(Cu, O)	37160
(Cu ₂ , Cl ₂)	65750
(Cu, Cl ₂)	51630
(Cu, Cl ₂ , aq)	62710
(Cu, O, SO ₃ aq)	55960
(Cu, O, N ₂ O ₅ aq)	52410
(Cu ₂ , S)	20240

CADMIUM.

(Cd, Cl ₂)	93240
(Cd, Cl ₂ , aq)	96250
(Cd, O, SO ₃ aq)	89500

SILVER.

(Ag ₂ , O)	5900
(Ag, Cl)	29380
(Ag, Br)	22700
(Ag, I)	13800
(Ag ₂ , O, N ₂ O ₅ aq)	16780
(Ag ₂ , O, SO ₃ aq)	20390
(Ag ₂ , S)	5310

MERCURY.

(Hg ₂ , O)	42200
(Hg, O)	30660
(Hg ₂ , Cl ₂)	82550
(Hg, Cl ₂)	63160
(Hg, Cl ₂ , aq)	59860

TIN.

(Sn, Cl ₂)	80790
(Sn, Cl ₂ , aq)	81140
(Sn, Cl ₄)	127240
(Sn, Cl ₄ , aq)	157160

GOLD.

(Au, Cl ₃)	22820
(Au, Cl ₃ , aq)	27270
(Au, Cl ₃ , HCl aq)	31800

III. WIRE RESISTANCES.

DIAMETER.	CROSS-SECTION.	RESISTANCE PER I M. OF WIRE.		
		Nickelin. Ω	Rheotan. Ω	Copper. Ω
0.10	0.008	51	60	2.23
0.15	0.018	22	26	0.99
0.20	0.031	13	15	0.56
0.25	0.049	8	9.5	0.36
0.30	0.071	5.6	6.7	0.247
0.35	0.096	4.1	4.9	0.182
0.40	0.126	3.2	3.7	0.139
0.45	0.159	2.5	2.9	0.110
0.50	0.196	2 0	2.4	0.089
0.55	0.238	1.68	1.99	0.074
0.60	0.283	1.41	1.67	0.062
0.65	0.332	1.20	1.42	0.053
0.70	0.385	1.04	1.23	0.045
0.75	0.442	0.90	1.07	0.040
0.80	0.503	0.79	0.94	0.035
0.85	0.568	0.70	0.83	0.031
0.90	0.636	0.63	0.74	0.028
0.95	0.709	0.56	0.66	0.025
1.0	0.785	0.51	0.60	0.022
1.1	0.950	0.42	0.50	0.018
1.2	1.131	0.35	0.42	0.016
1.3	1.328	0.30	0.35	0.013
1.4	1.539	0.26	0.31	0.011
1.5	1.767	0.23	0.27	0.010
1.6	2.009	0.199	0.235	0.009
1.7	2.270	0.176	0.208	0.008
1.8	2.545	0.157	0.186	0.007
1.9	2.835	0.141	0.167	0.0062
2.0	3.141	0.127	0.150	0.0056
2.1	3.464	0.115	0.137	0.0051
2.2	3.801	0.105	0.124	0.0046
2.3	4.155	0.096	0.114	0.0043
2.4	4.524	0.088	0.105	0.0039
2.5	4.909	0.081	0.096	0.0036
2.6	5.309	0.075	0.089	0.0033
2.7	5.725	0.070	0.082	0.0031
2.8	6.158	0.065	0.077	0.0028
2.9	6.605	0.061	0.072	0.0026
3.0	7.069	0.057	0.067	0.0025

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